UNCLASSIFIED

AD 273 971

Reproduced
by the

ARLINGTON HALL STATION
ARLINGTON 12, VIRGINIA

UNCLASSIFIED

DISCLAIMER NOTICE

THIS DOCUMENT IS BEST QUALITY PRACTICABLE. THE COPY FURNISHED TO DTIC CONTAINED A SIGNIFICANT NUMBER OF PAGES WHICH DO NOT REPRODUCE LEGIBLY.

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

62-3-1

CATALOGED BY ASTIA
AS AD No. 273971

273971

FUEL CELL

RESEARCH & DEVELOPMENT

RESEARCH ON LOW TEMPERATURE FUEL CELL SYSTEMS

SUMMARY REPORT - SECTION II
(REPORT NUMBER 19)
NOVEMBER 1, 1959 TO NOVEMBER 30, 1961

CONTRACT NUMBER DA-44-009-ENG-3771

U.S. ARMY

ENGINEER RESEARCH AND DEVELOPMENT LABORATORIES

FT. BELVOIR, VIRGINIA

AIRCRAFT ACCESSORY TURBINE DEPARTMENT

GENERAL ELECTRIC

RESEARCH ON LOW TEMPERATURE
FUEL CELL SYSTEMS

BY

RESEARCH LABORATORY

AND

AIRCRAFT ACCESSORY TURBINE DEPARTMENT

SUMMARY REPORT - SECTION II

(REPORT NUMBER 19)

NOVEMBER 1, 1959 TO NOVEMBER 30, 1961

CONTRACT NO. DA-44-009-ENG-3771

U.S. ARMY ENGINEER
RESEARCH AND DEVELOPMENT LABORATORIES
FT. BELVOIR, VIRGINIA

GENERAL ELECTRIC COMPANY
AIRCRAFT ACCESSORY TURBINE DEPARTMENT
LYNN, MASSACHUSETTS

TABLE OF CONTENTS

Page

Introduction 1

Summary 2

Exhibit B 3

Task II Oxygen Electrode 5

1.0 Introduction 5
Thermodynamic Principles and Application 6
Criteria of Thermodynamic Reversibility 10

2.0 Experimental Approach 13
Definition of Polarization 13
Types of Oxygen Electrodes and Fuel Cell Structures Investigated

3.0 Experimental Results 19
Effect of Different Catalysts for the Oxygen Electrode in the Ion-Exchange Membrane Cell 26

4.0 Open Circuit Voltages Greater than the Theoretical Values 47

5.0 Discussion of Results 51

6.0 Experimental Observation 52

7.0 Fundamental Thermodynamic Facts 53

8.0 Fundamental Electrochemical Facts 53

9.0 Review of the Theories of the Oxygen Electrode Irreversibility 63

10.0 Recommendations For Future Work 80

11.0 Literature References 81

12.0 Appendix A 86

13.0 Appendix B 94

14.0 Appendix C 98

15.0 Acknowledgement 103

INTRODUCTION

This is a technical progress report of a research program on low temperature fuel cell systems conducted by the General Electric Company under Contract No. DA-44-009-ENG-3771 with the U.S. Army Engineer Research and Development Laboratory. Original work was initiated in October 1958 under the title "Materials Study Redox Fuel Cell" and was extended in September 1959 under the title "Redox and Related Fuel Cell Systems." In April 1960, work on the Redox system was concluded and summarized in Report No. 9; however, work associated with the direct conversion of fuels was expanded to its present concept. Work has continued under the title "Research on Fuel Cell Systems" as outlined in "Exhibit E."

The objective of this program is to develop a technology which will serve as the basis for design and fabrication of fuel cell packs for ground power units and power for traction devices for military applications. A primary aim is the more efficient utilization of conventional liquid hydrocarbon fuels. Close guidance and approval of the direction of this work is given by Mr. E. Cogswell of the U.S. Army Research and Development Laboratories, Ft. Belvoir, Virginia.

These progress reports are issued on a bi-monthly basis and special summary reports will be issued as indicated. The reader should recognize that this is a progress report covering a particular period of time. The experiments reported are factual, but not necessarily complete, and any conclusions must be considered tentative until a summary report is issued. Comments and suggestions on these reports are most welcome.

SUMMARY

This report describes the research work conducted under the U. S. Army Engineer Research and Development Laboratories Contract No. DA-44-009-ENG. 3771, Task II. The objectives of this program were to determine the cause and the mechanism of the polarization losses associated with the oxygen electrodes for fuel cells operating in acidic and alkaline media.

Polarization behavior of the oxygen electrode and of the hydrogen-oxygen fuel cells using a variety of catalytic electrodes in acidic, alkaline and solid-ion-exchange membrane electrolytes was investigated.

On the basis of the experimental data presented here, it is concluded that (a) under the practical operating conditions of a hydrogen-oxygen fuel cells, an IR-free, steady state emf greater than approximately 0.93V is not likely to be achieved. (b) The IR-free polarization loss of approximately 0.3V appears to be associated with some specific property of the hydrogen-oxygen fuel cells since it is apparently unaffected by the usual rate or kinetic parameters including the pH, temperature, partial pressures of gases, or the chemical nature of the catalytic surfaces. This polarization loss is tentatively attributed to the inherent, unavoidable pH gradients associated with current flow. An energetic interpretation in terms of established thermodynamic treatment is suggested. (c) Platinum black appears to be the best catalyst known to date for the oxygen electrode, and judging from the essentially zero slope of the IR-free linear polarization plots covering a fairly large range of current density, it would appear that a catalyst more effective than platinum black is not likely to be found since the inherent thermodynamic irreversibility cannot be reduced or eliminated by catalysts. (d) Various existing theories of the irreversibility of the oxygen electrode have been reviewed and it is concluded that none of these can satisfactorily explain all the experimental observations concerning the open-circuit behavior of the oxygen electrode. A tentative interpretation based on the double layer capacitance effects is suggested for the various effects associated with the irreversibility of the hydrogen-oxygen fuel cells at or near the open-circuit conditions. It is shown that under certain conditions and by properly buffering the pH in the vicinity of each electrode, open-circuit voltages greater than 1.23V can be attained. The additional voltage, however, cannot apparently be used as a source of steady emf or electrical energy. Recommendations for further work are outlined.

SUMMARY (Cont'd)

This is Section II of the Summary Report "Research on Low Temperature Fuel Cell Systems." Section I was distributed previously in December, and included the work accomplished at the Research Laboratory under Drs. L.W. Niedrach and T.W. Grubb.

This Section II includes the work covered by the Aircraft Accessory Turbine Department Fuel Cell Engineering Laboratory by Dr. P.V. Popat. Both Sections I and II are issued under Report Number 19.

U.S. ARMY ENGINEER RESEARCH AND DEVELOPMENT LABORATORIES

"EXHIBIT E"
RESEARCH ON FUEL CELL SYSTEMS

19 September 1960

The research to be conducted under this Exhibit E provides for the continuation of research on "other fuel cell concepts" as described in "Amended Exhibit D" dated 20 April 1960, and as provided for in paragraph 5 of "Exhibit D" dated 18 August 1959.

Research shall be conducted on the following tasks:

TASK I Study of the adsorption and kinetics of the oxidation of hydrocarbons on different catalyzed electrode surfaces, both in acid and alkaline media.

1. Development of electrodes of different structures, their activation and incorporation of different catalysts.

2. Investigation of the properties of the catalyzed electrodes, developed in 1, concerning the oxidation of pure gaseous hydrocarbons by conducting half cell studies.

   a. Study of the adsorption of hydrocarbons and their reaction products on the electrode surfaces.

   b. Study of the oxidation kinetics of hydrocarbons and their reaction products on the electrode surfaces.

   c. Study of the influence of additives to fuel and electrolyte and influence of pH and process variables (i.e. temperature, pressure, concentration, etc.) on the reaction rates.

3. Development of improved electrolyte structures.

4. Evaluation of these electrolytes in test cells, using the fuel electrodes, developed in 2, concerning:

   a. The electrical conductivity.

   b. The mechanical strength and gas-permeability of the electrolyte structures of varying thickness.

c. The influence of reaction by-products (H_2O, CO_2, precipitates) on the conductivity, mechanical strength, etc., determined in long term test.

5. Study of the possibilities of the direct oxidation of heavier liquid hydrocarbons and mixtures thereof according to 2. This task to be initiated pending the completion of 1 through 4 above.

TASK II Study of the kinetics of the oxygen electrode both in acid and alkaline media.

1. Investigation of the rate limiting step in the overall reduction of oxygen on different catalyzed electrode surfaces.

2. Study of the effect of reaction products on the kinetics of the oxygen electrode. (i.e., the formation of hydrogen peroxide and metal oxides).

3. Study of the influence of additives to the oxygen and electrolyte and the effect of pH and process variables on the kinetics of oxygen reduction.

TASK II - OXYGEN ELECTRODE

1.0 Introduction

One of the major problems in the development of practical hydrogen-oxygen or hydrogen-air fuel cells is encountered at the oxygen electrode. It has been known for a long time that at ordinary temperature, the oxygen-electrode attains its rest potential (open circuit voltage) only sluggishly and more or less irreproducibly depending on the physical and chemical nature of the electrode material, and does not exhibit the true reversible potential even in the presence of the best known electrocatalyst such as platinum black.

Repeated attempts over the years by various investigators to achieve this thermodynamically reversible potential and to maintain it over a significant period of time have all been unsuccessful. Another and perhaps more serious difficulty from operational point of view is presented by the fact that the oxygen electrode polarizes rather rapidly even at small current densities as indicated by its potential measured with respect to a reference electrode.

In spite of a considerable amount of published work on the kinetics of the electrochemical reduction of oxygen at catalyzed as well as uncatalyzed cathodes, very little is known concerning the exact cause and the mechanism of the voltage or energy dissipation associated with the oxygen electrode on open circuit or under small current flow conditions. Clearly this information is essential before any logical steps can be taken to reduce this voltage or energy dissipation.

Realizing the importance of this problem for fuel cell systems, a comprehensive program aimed at achieving a better understanding of the exact cause and mechanism of the polarization loss exhibited by the oxygen electrode has been initiated. This report gives a comprehensive summary of the theoretical and experimental work performed by one scientist during the period of April 15, 1960 to October 15, 1961 under the Contract No. DA-44-009-ENG-3771 from the Engineer Research and Development Laboratories, U.S. Army. For details, the preceding Porgress Reports (No. 11 to 17) should be examined.

Any theoretical approach or interpretation of experimental results suggested here must be considered tentative at present since further work must be performed before definite conclusions can be made. Apart from the theoretical implications resulting from this study, the experimental results presented here are believed to have significant implications for the practical application of fuel cell systems involving the oxygen or air electrode, since they suggest a maximum upper limit of the available E.M.F. from a hydrogen-oxygen fuel cell using aqueous electrolytes and operating at practical current densities.

Thermodynamic Principles and Application

It is now well established that the standard free energy change, ΔG^o for the overall reaction:

$$H_2\ (g) + \tfrac{1}{2}\ O_2\ (g) \rightleftharpoons H_2O\ (\ell) \qquad (1)$$

under thermodynamic equilibrium conditions, with each reactant and product at unit thermodynamic activity is 56,690 calories or -2.458 volt-faradays per mole of liquid water formed at 25°C (1).

Thermodynamic Principles and Application

Assuming that two faradays are transferred to the external circuit per mole of H_2 reacted electrochemically, the standard emf, E^o, associated with reaction (1) carried out electrochemically is 1.229V at 25°C. For electrochemical investigations, it is convenient to arbitrarily divide this total E.M.F. into two half-cell potentials as follows:

The anodic half cell reaction at equilibrium may be written as:

$$2H^+ \ (aq) + 2e \ \underset{\text{Catalyst}}{\overset{H_2O}{\rightleftharpoons}} \ H_2 \ (g) \qquad (2)$$

This half cell reaction has been arbitrarily selected as the basis for the universal primary standard reference electrode and the potential associated with it at unit activity of the reactant (s) and product is assigned, again arbitrarily, the value of 0.0000 V at all temperatures. The dependence of the reversible potential V, of the hydrogen electrode on the activity, (a_i), of the reactant and product is given by the classical Nernst equation:

$$V_{H^+/H_2} = V^o_{H^+/H_2} + \frac{RT}{\eta F} \ln \frac{(H^+)}{(H_2)^{\frac{1}{2}}} \qquad (A)$$

where $V^o_{H^+/H_2}$ is the standard hydrogen electrode potential (= 0.00V) and the other symbols have the usual significance.

The other half cell reaction involving the cathodic reduction of oxygen is usually written in several different ways depending on the pH of the bulk electrolyte used. In an alkaline or neutral electrolyte, the complete reduction (a four electron change per mole of O_2 reacted) is usually written as:

$$\tfrac{1}{2} O_2 + H_2O + 2e \rightleftharpoons 2OH^-; \qquad V^o_{O_2/OH^-} = 0.401V \qquad (3)$$

whereas in acidic electrolyte the half-cell reaction is assumed to follow:

$$\tfrac{1}{2} O_2 + 2H^+ + 2e \rightleftharpoons H_2O \ (\ell); \quad V^o_{O_2/OH^-} = 1.229V \qquad (4)$$

The dependence of the reversible emf of the oxygen electrode on the activity of the reactants and the products is then given by the appropriate Nernst equation. Thus, for the half-cell reactions (3) and (4) respectively, the corresponding Nernst equations are:

$$V_{O_2/OH^-} = 0.401 + \left(\frac{RT}{\eta F}\right) \ln \left(\frac{(O_2)^{\frac{1}{2}} \ (H_2O)}{(OH^-)^2}\right) \qquad (B)$$

NOTE: The sign convention for the electrode potentials used here is the standard European (Gibbs - Stockholm) convention and the various half-cell reactions and Nernst equations are written in conformity with this convention.

Thermodynamic Principles and Application (Cont'd)

$$V_{O_2/OH^-} = 1.229 + \frac{RT}{nF} \quad \frac{(O_2)^{\frac{1}{2}} (H^+)^2}{(H_2O)} \qquad (C)$$

However, if the molecular oxygen is first reduced to a peroxide species at the cathode and if this electrochemical step, namely:

$$O_2 + 2H^+ = 2e \underset{\text{media}}{\overset{\text{acidic}}{\rightleftharpoons}} H_2O_2 \qquad V^o_{O_2/H_2O_2} = 0.682V \qquad (5)$$

$$\text{or} \quad O_2 + H_2O + 2e \underset{\text{media}}{\overset{\text{alkaline}}{\rightleftharpoons}} HO^-_2 + OH^- \qquad V^o\ O_2/HO^-_2 = -0.074V \qquad (6)$$

is potential determining, the corresponding Nernst equation for the half-cell reaction (5) is:

$$V_{O_2/H_2O_2} = 0.682 + \frac{RT}{nF} \ln (O_2)(H^+)^2 / (H_2O_2) \qquad (D)$$

and for (6) is:

$$V_{O_2/OH^-} = -0.074 + \frac{RT}{nF} \ln \frac{(O_2)(H_2O)}{(H_2O^-)(OH^-)} \qquad (E)$$

the standard thermodynamic potentials associated with different modes of oxygen reduction at pH values of 0, 7, and 14 respectively are given in Table I.

TABLE I

Thermodynamic Potentials (in volts) for Oxygen Reduction
Reactions at 25°C (Std. Hydrogen Electrode = 0.000V)
Based on the data from latimer (1) collected by Pawlowski (2)

Reaction	V^o (pH = 0)	V^o (pH = 7)	V^o (pH - 14)
Four Electron Step			
$O_2 + 4H + 4e \rightleftharpoons H_2O$	+1.229	+0.815	+0.401
Two Electron Steps			
$O_2 + 2H^+ + 2e \rightleftharpoons H_2O_2$	+0.862	+0.268	-0.076
$H_2O_2 + 2H^+ + 2e \rightleftharpoons 2H_2O$	+1.77	+1.36	-0.88
One Electron Step			
$O_2 + H^+ + 2e \rightleftharpoons HO_2$	-0.13	-0.54	-0.56
$HO_2 + H^+ + 2e \rightleftharpoons H_2O_2$	+1.5	+1.1	+0.4
$H_2O_2 + H^+ + e^- \rightleftharpoons OH + H_2O$	+0.72	+0.31	-0.24
$OH + H_2O + H^+ = \rightleftharpoons 2H_2O$	+2.8	+2.4	+2.0

Thermodynamic Principles and Application (Cont'd)

The equilibrium values of the potentials of the oxygen electrode, the peroxide electrode and the hydrogen electrode as a function of pH at 25°C and one atmosphere pressure reported by Latimer (1) are given in Figure (1).

In splitting the thermodynamic EMF of reaction (1) into hydrogen and oxygen electrode potentials discussed above, "a non-thermodynamic assumption has been covertly made" according to Ives and Janz (3). The assumption is that it is possible to determine the activity of a single ionic species; this is not possible, "unless more significance is attributed to the Debye-Huckel calculation than is strictly justifiable." All that can be determined is a mean ion activity

$$a_{\pm} = \left(a^{\nu_+} + a^{\nu_-}\right)^{\frac{1}{\nu}}$$

for an electrolytic solute which provides on dissociation, $\nu+$ cations and $\nu-$ anions "per mole", where $\nu = (\nu+) + (\nu-)$. This is related to determinable molalities $M_{\pm}$ by:

$$a_{\pm} = (\nu_{\pm})\,(M_{\pm})$$

Where $\nu_{\pm}$ is a mean molar ionic activity coefficient which approaches unity at infinite dilution. This activity coefficient is a function of the ionic interactions which are responsible for the non-ideality of the solute. These naturally occur predominantly between ions of opposite sign of charge, and in very dilute solutions they are coulombic in nature and are calculable. In stronger solutions, specific ionic properties must enter, together with such solute-solvent interactions which can no longer be regarded as independent of concentration. "It is thus clear that the task of interpreting activity coefficients, let alone their dependence upon temperature involves complex physiochemical problems, except under near ideal conditions. It is also obviously a matter of doubt whether any real significance can be attached to a single ion activity coefficient. It has nevertheless been unavoidable, in splitting an EMF into electrode potentials to make some arbitrary assumption such that:

$$a_{+} = a_{-} = a_{\pm} \qquad (3)$$

In applying the thermodynamic principles to individual electrode potential involving charged particles, other fundamental difficulties arise. For substances composed of uncharged atmos or molecules, the concept of chemical potential is of immense value because it comprehends all the factors which determine their behavior. Thus, it is a universal criterion of equilibrium within a system that the chemical potential, μ_i, of any component $_i$ shall, like pressure and temperature, have a uniform value in all parts of the system. The question arises, how can this function be adapted to deal with the electrochemical problem in hand? "In the first place, it must be noted that chemical potential is essentially a thermodynamic function with the dimensions of energy per mole; it does not deal with individual atoms or molecules. If it turns out to be permissible to discuss the "chemical potential of sodium ions"; for example, this must always mean a thermodynamic function relating to a particular macroscopic system which contains these ions, and must retain the dimensions of energy per mole.

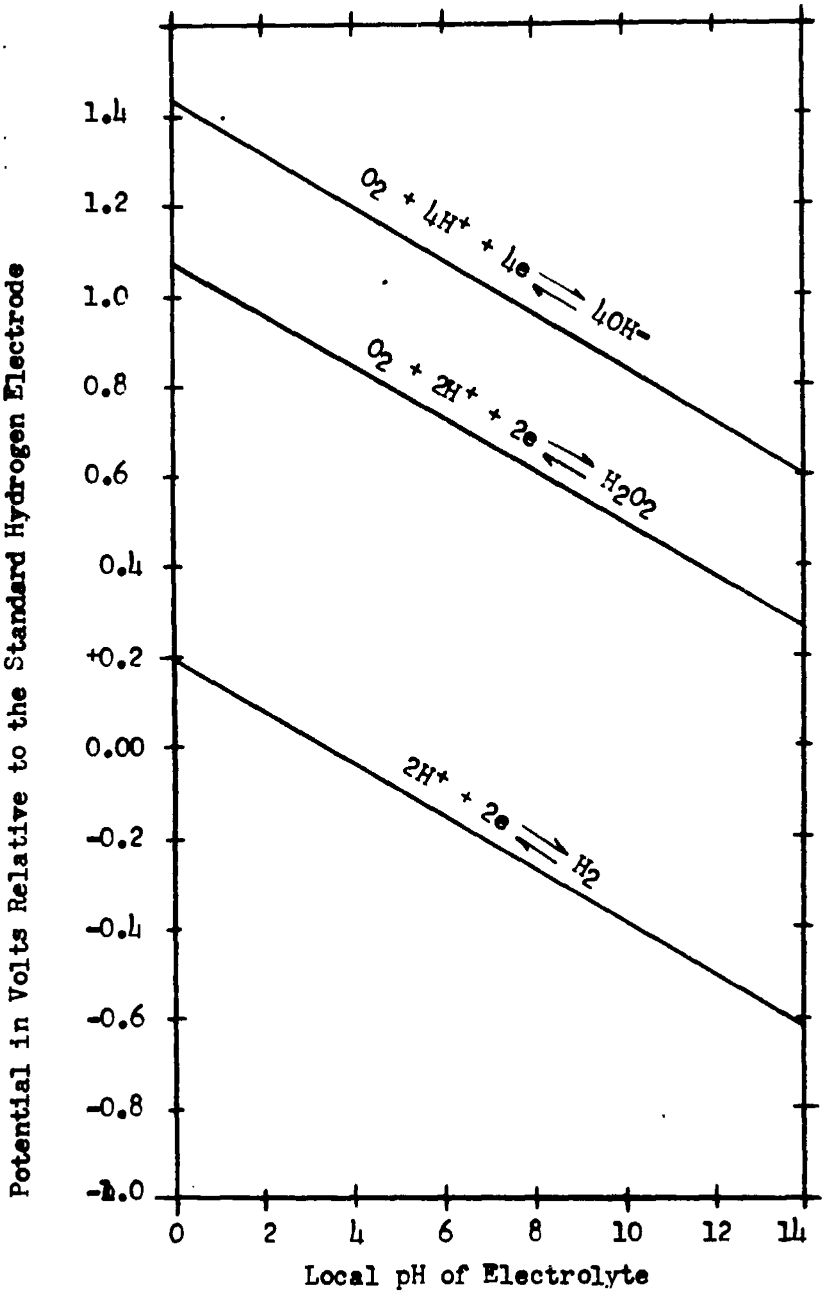


Figure 1

pH Dependence of the Reversible Potentials of the Hydrogen Electrode, the Oxygen Electrode and the Oxygen-Peroxide Electrode at 25°C in Aqueous Electrolytes

In fact he concludes that any ion which is present in a concentration lower than 10^{-10}M can have no appreciable effect on the electrode potential, and as Langumir (4) has stated, Haber's arguements are "absolutely unassailable." With these "microscopic" quantities of the "potential determining species", the relative size or surface area of the electrode at which the potential is established also becomes of increasing importance since it is the effective concentration, or strictly the activity at the electrode which must determine the relevant electrode potential. With decreasing ionic population at the electrode, at some stage, it will become mechanistically impossible for the ions to control the electrode potential.

Thus, we are in a delicate situation where we must define, for a given system as to when exactly the realm of classical reversible thermodynamics, dealing with bulk macroscopic quantity ends and that of the irreversible thermodynamics begins. Muller (5) has stated that for polarographic studies at a dropping mercury ("micro") electrode a minimum concentration of about 10^{-6}M of both the oxidant and the reactant is necessary to make the observed potential thermodynamically significant.

Here it may be noted that the Nernst equation is not applicable to a chemically or electrochemically irreversible process (6,7) and it becomes necessary before applying the Nernst equation, to make sure that the process under consideration is at or near the reversible equilibrium conditions. That this could be a difficult task is effectively illustrated by the noted irreversibility of the hydrogen electrode under many, as yet undefined, conditions. According to Potter (8) the somewhat strange circumstances that the hydrogen electrode reaction can be sufficiently reversible to merit adoption as a standard of reference and yet, under different conditions (not yet defined or known) be highly irreversible can greatly affect the implications of the electromotive series when especially applied to aqueous solutions containing hydrogen ion. Thus, for instance, in attributing the irreversibility of the hydrogen-oxygen fuel cell reaction, represented by equation (1) to the oxygen electrode, it becomes necessary to establish beyond doubt that the hydrogen electrode under these conditions behaves reversibly. It would appear at present that it may be difficult to establish this unequivocally when the two electrodes are very closely spaced and operating in the same bulk electrolyte, particularly with the fuel cells type systems.

Criteria of Thermodynamic Reversibility

A reaction occuring in an isolated, macroscopic system is considered to be at thermodynamic equilibrium when the rate of the forward reaction becomes equal to the rate of the reverse reaction so that the net rate of change in the concentration of any of the participating species as a function of time is zero.

Im the second place, it is necessary to enquire whether the definition of chemical potential

$$\mu_i = \left(\frac{\partial G}{\partial i}\right)_{t,P,N_j}$$

allows it to be applied to ions at all. This expression can be translated as the proportional increase in free energy of a system resulting from the addition to it of dn_i mole of components, i, the number of moles of all other components, n_j , and the temperature and pressure being kept constant. It is impossible to add a single kind of ion to any system, in which at equilibrium no significant departure from electro neutrality is possible. Each kind of ion is partnered by its oppositely charged counterparts, so that if ions are to be added to a system, at least two kinds of ions must be added simultaneously. This does not, however, invalidate the definition because dG is a perfect differential, -------- but it does mean that the chemical potential of a single kind of ion can never be separately determined." (3).

It is evident from the about discussion that, in principle, no single electrode potential can be known, nor any thermodynamic property of a single ionic species can be unequivocally determined. Yet such quantities are widely used in electrochemical calculations. For this to be acceptable, appropriate precautions and safeguards should always be adopted. Thus, in discussing any single electrode in such "non-thermodynamic terms" the relevant precaution suggested by Ives and Janz (3) is to answer the question: Can this electrode be combined with another to give a reversible cell with an EMF which is thermodynamically calculable? Or, can this electro-chemical potential, or ionic activity, be combined with another similar term to give a physically measurable quantity?

It would appear that these questions are of primary importance in the measurement of individual electrode polarization and its interpretation, particularly in the case of the more or less irreversible electrodes such as the hydrogen and oxygen electrodes under consideration here.

Another fundamental difficulty which can significantly affect the thermodynamic analysis and interpretation of experimental results is encountered in determining the conditions under which the appropriate Nernst equation for each electrode (e.g. equations A to E) is applicable. It is obvious that as the activity or the effective concentration of one of the potential determining species becomes vanishingly small, the electrode potential as calculated from the Nernst equation becomes meaningless since it tends to go off to infinity. At present there is apparently no general agreement as to the lowest concentration of the electroactive species which must be present for the measured potentials to be thermodynamically meaningful in terms of the Nernst equation. This problem assumes a major importance in determining for instance, the contribution of the peroxide mechanism in the oxygen electrode polarization at catalytically active electrodes which can decompose any peroxide species, if involved , as fast as produced, thereby reducing the peroxide concentration at the electrode to substantially zero value. This is an old electrochemical problem as first illustrated by Ostwald's calculation that there is only about one silver ion per liter in a silver solution to which sufficient potassium cyanide has been added (4). Haber argued that the potential of the silver electrode cannot possibly be determined by the presence of such small concentration of ions which in this case is as low as 10^{-24} molar

Criteria of Thermodynamic Reversibility - Cont'd

Extending this definition to an electrochemical half-cell or single electrode process involving ions and electrons (which can be made only at the expense of some of the thermodynamic rigor as discussed earlier), the electrode would be considered at equilibrium when the cathodic rate is equal to the anodic rate so that the net current at the electrode is zero. The "reversible" current at the electrode under this equilibrium condition is known as the exchange current, i_o, which is considered to be a characteristic thermodynamic property of the electrode. The true or absolute value of this quantity for any given electrode can never be measured in practice since any attempt to measure it will necessarily distrub the true equilibrium conditions. In practice, therefore, it becomes necessary to resort to some kind of an extrapolation and obtain an "apparent exchange current." The difference between the true and the apparent exchange current will depend upon the particular system under consideration, the method of measurement, the method of plotting the data and the method of extrapolation used. In any case, however, there will always remain a certain degree of uncertainty concerning the "apparent exchange current" since the true value cannot be known.

Experimentally, perhaps a more fundamental electrochemical parameter is the emf associated with an overall electrochemical reaction or the potential associated with an electrode process. The measured potential difference can be identified with the reversible emf or electrode potential provided the measured emf (a) remains invariant as a function of time (b) agrees with the thermodynamically calculated value based on the Nernst equation assuming that the relevant activities at the electrode are known (c) the variation in the activities obey the Nernst equation, and (d) the same reversible emf is obtained while approaching the open-circuit voltage from either direction.

When the above criteria are not satisfied, it is an indication that the cell or electrode under consideration does not, probably, behave in a reversible manner. In addition, the following criteria of irreversibility of a cell (9) may be noted: (a) Fluctuation in the emf (b) Apparently identical electrodes in the same solution under apparently the same conditions give different values on emf (c) Changes in the emf on agitation (d) The potential does not rapidly return to the equilibrium value after polarization. When the measured emf at zero net current (that is, the rest potential) does not agree with the reversible value as judged by the above criteria, the interpretation of the measured open circuit voltage becomes an extremely difficult problem as will be shown in the case of the oxygen electrode.

Although the classical thermodynamic methods are independent of time as a variable, in practice the time factor does enter into all thermodynamic investigations of real systems, because starting from non-equilibrium conditions, certain amount of time is required before the system will attain a state of equilibrium. This is the place where the kinetic parameters involving catalysis enter into the behavior of the electrochemical processes involving gas electrodes, specially hydrogen and oxygen electrodes. This is in sharp contrast to reversible redox reactions e.g. Fe^{++} (aq. soln.) $\rightleftharpoons$ Fe^{+++} (aq. soln), which occur entirely in the solution phase. For electrodes involving molecular hydrogen or oxygen, the homogeneous exchange equilibrium such as H_2 (aq. soln) $\rightleftharpoons$ $2H^+$ (aq. soln.) + $2\bar{e}$ is not established since the exchange current for the homogeneous (solution phase) reaction is negligible.

Criteria of Thermodynamic Reversibility - Cont'd

If an inert or indifferent metal electrode is placed in the solution containing hydrogen molecules and hydrogen ions, the inert electrode will not assume the potential defined by the above equilibrium for the hydrogen electrode, since the equilibrium does not exist. In this case the measured open circuit voltage will have little or no thermodynamic significance as far as the hydrogen electrode is concerned. It is thus clear that something more is required of the metal than to give or receive electrons. "It must catalyze the equilibrium" (10). With the hydrogen electrode this may be written as: $H_2 \rightleftharpoons 2H$ (adsorbed on metal catalyst) $\rightleftharpoons 2H^+$ (aq. soln.) $+ 2e^-$. Therefore the catalytic property of the electrode in establishing the above equilibria becomes very important. This property must assume greater significance for the oxygen electrode since energetically the adsorption of O_2 and its dissociation into atoms or the reverse of these is likely to be more difficult in the case of oxygen. It should be emphasized that an inert or indifferent electrode is capable of remaining in a state of non-equilibrium for indefinite time, whereas a reversible electrode is an electrode for which the state of electrochemical equilibrium is essentially a state of true thermodynamic equilibrium. In practice, the difference between a truly reversible electrode and an indifferent electrode is gradual and will depend, among other things on the catalytic activity of the electrode material. However, it is difficult to define exactly where the electrode ceases to be reversible and where the inert or indifferent electrode takes over, since even a perfectly inert electrode will exhibit certain potential, though not necessarily due to the reaction under consideration. For fuel cell applications, the indifferent electrodes, e.g. mercury or bright-smooth platinum are considered to be relatively minor in importance and the experimental work is primarily restricted to catalytically active surfaces of materials like platinum black that show high exchange rates for the reaction under consideration.

2.0 EXPERIMENTAL APPROACH

Definition of Polarization

Electrochemical polarization associated with a given reaction such as reaction (1) is defined here as the difference between the reversible thermodynamic emf associated with that overall reaction and the measured value of the emf of the complete cell at a given current density. Symbolically $\eta_{Cell} = E^{o}_{rev.} - E_{m}$. Where η cell is the total cell polarization associated with the reaction (1) carried out in a fuel cell, E^{o}_{rev} is the standard reversible emf for reaction (1) at 25°C the standard reversible emf will be 1.229V, as shown in Figure I provided both the electrodes function or can be made to function at the same pH. For the purposes of experimental investigation, the total cell polarization is usually divided into the following types:

$$\eta_{cell} = \eta_o + \eta_c + \eta_{H_2} + \eta_{O_2}$$

where η_o represents the ohmic polarization due to the internal resistance of the cell, η_c represents the concentration polarization due to changes in the activities of the reacting species at each electrode, η_{H_2} and η_{O_2} represent the so-called activation or chemical polarization associated with the hydrogen electrode and the oxygen electrode respectively.

Definition of Polarization (Cont'd)

It can be safely assumed, on the basis of extensive published work, as well as our own work reported later, that the internal resistance of the cell can be determined fairly accurately by several independent methods and corrected for: $\eta \mathrm{cell} - \eta_o = \eta_c + \eta_{H_2} + \eta_{O_2}$.

The determination of the contribution of η conc., η_{H_2} and η_{O_2} respectively to the overall cell polarization (corrected for IR) presents a difficult experimental problem. It can be safely assumed, on the basis of the experimental evidence presented later, that the concentration polarization associated with the transport of the molecular hydrogen and oxygen to the electrode can be substantially eliminated by proper experimental conditions. The concentration polarization associated with the ionic species produced at each electrode, however, is not at all easy to measure experimentally, or to calculate theoretically, particularly with the fuel cell systems. The reasons for this will be discussed in detail in the discussion section, but it is necessary to point out here that both the hydrogen and the oxygen electrode potentials are pH dependent through the Nernst equation, and that since, in effect, the anodic reaction produces an acid and the cathodic reduction produces a base, the two electrodes cannot function at the same pH (at least in principle) at any finite faradaic current. It should be pointed out that because of the high catalytic activity and large surface areas of the electrodes, they have a great ability and large capacity to specifically adsorb the ionic species produced at each electrode, thereby changing the effective pH at each electrode. There is, at present, no way of accurately measuring the pH at each electrode (except by measuring the potential which is the parameter we want to investigate and interpretate). It is also not possible at present to calculate with any degree of accuracy or certainty the pH changes at each electrode or ionic concentration polarization using the Fick's law of diffusion and the relevant ionic diffusion coefficients since the following requirements must be fulfilled for the Fick's law to be applicable: (a) "Free diffusion" under pure concentration gradient (b) Absence of any potential (electrical) gradients and specific adsorption forces (c) Idealized ions at infinite dilution, which in practice demands a large concentration of an indifferent electrolyte to carry the bulk of the ionic current and only a small concentration of the electroactive species so that the transference or migration current can be reduced to a negligible value. (d) The thickness of the diffusion layer and the value of the diffusion coefficient of the relevant ionic species must be known. When these requirements are examined in case of fuel cell systems, it becomes evident that none of these requirements are satisfied. Thus, for instance, practically all the ionic transport occurs under electrical gradient, especially in the case of the ion-exchange membrane fuel cells and that at each catalytic electrode there are powerful ionic interaction or adsorption forces. There is no inert electrolyte present and the ionic species carrying the current are all electroactive. The thickness of the diffusion layer is unknown because the two electrodes are very closely spaced (less than 0.1 cm as discussed below). This is particularly true for ion-exchange membrane fuel cells where the current is transported by modes other than pure diffusion. Finally the diffusion coefficients for the highly concentrated acids and bases generally employed in fuel cells are not calculable since in concentrated solutions, the diffusion coefficient depends markedly on concentration.

Definition of Polarization (Cont'd)

For these reasons, the measurement or calculation of the contribution of the ionic concentration polarization at each electrode in actual fuel cell systems is not possible at present and considerable amount of theoretical and experimental work will be necessary before satisfactory solution of these problems can be found.

The problem of unambiguously determining η_{H_2} or η_{O_2} for the hydrogen-oxygen fuel cells operating in the same bulk electrolyte appears to be equally difficult. Apart from the theoretical problems involved in splitting the total emf into individual electrode potentials as discussed under thermodynamic considerations, there are many experimental problems which have not yet been solved. Thus for instance, in order to calculate η_{H_2} or η_{O_2} we must know the effective activity of the ionic species at the electrode so that the actual reversible electrode potential can be calculated using the appropriate Nernst equation. The difficulties encountered are discussed under the concentration polarization. Each electrode is pH dependent and in close proximity ($<$ 0.1 cm) of the other electrode. Therefore any pH dependent reference electrode (such as the standard hydrogen electrode) is clearly unsuitable as a reference electrode unless the relevant ionic distribution (or gradient) is known. It is possible to use other reference electrodes such as a saturated calomel electrode but there are several practical problems and ambiguities to be resolved. The experimental results obtained with several types of references electrodes are presented in the section on experimental results where the experimental problems associated with the use of reference electrodes are discussed in greater detail. From these preliminary results and on the basis of the above discussion, it is tentatively concluded that, for the hydrogen-oxygen fuel cell systems, reliable methods of measuring η_{H_2} and η_{O_2} are not yet established and that, therefore, η_{H_2} and η_{O_2} cannot be separated unequivocally from each other or from η_c. The immediate solution is to treat these quantities together. It should be emphasized, however, that this is only a temporary expedient and the importance of evaluating the reliability of the known reference electrodes or devising new methods of measuring individual electrode potentials in an operating hydrogen-oxygen fuel cell should by no means be minimized. In the meantime, it is believed that the total cell polarization (after IR correction) is an unambiguous and reliable physical quantity and gives very valuable information both from theoretical and experimental points of view as will be shown in this report. In their book on Reference Electrodes, Ives and Janz (11) recognize this approach as fundamentally sound and in fact, inherently more reliable. Here it may be of interest to quote their exact words: "The question of single electrode potentials may now be raised again. Fundamentally indeterminate as they are, they will have to be expressed on some arbitrarily invented scale. It may well be asked, why is it necessary to do this at all? Would it not be better to stick to the quantities which can be measured unambiguously, namely, the emf values for complete cells? The answer is that it undoubtedly would be better and that it should be done on every occasion." This appears to be of particular significance for the hydrogen and oxygen electrodesof fuel cells. Therefore, the majority of data presented here are for the emf values of complete cells unless otherwise stated.

Types of Oxygen Electrodes and Fuel Cell Structures Investigated

During the course of this contract work, the oxygen electrode behavior was investigated using the following types of fuel cell structures or designs.

TYPE I A. The General Electric Company Ion-Exchange membrane fuel cells made from sulfonated phenol-formaldehyde polymer membrane with the catalytic film electrodes integrally bonded to each side of the polymer matrix. After manufacture, the membranes were completely leached out in distilled water and the pH of the leached membrane was about 3.5. The total cell thickness (spacing between the electrodes) was about 0.06 cm including the thickness of each electrode which was about 0.003 cm. The geometric area of the cells investigated was either 10 cm^2 or 100 cm^2, though in some cases polarization curves were compared with larger cells (say 100 $in.^2$). Hydrated protons are assumed to be the only ionic species involved in the ionic transport through the membrane in which anions are fixed in the polymer matrix. Various catalysts were used for the oxygen electrode.

TYPE I B. Catalytic film electrodes held on two separate cationic exchange membranes which were separated by aqueous solution of sulfuric acid of different concentration. The spacing between the membranes was about 0.1 cm. These studies were carried out in connection with another project with G.E. funds, but the polarization characteristics are summarized here because they are significant for the behavior of the oxygen electrode.

TYPE II Free Aqueous electrolytes (a) held in an inert matrix such as filter paper (b) equilibrated in ion-exchange membrane cells.

A. Acid Electrolyte (2N H_2SO_4)
B. Alkaline Electrolyte (6N or 30% KOH)

The ion-exchange matrix used for fixing the electrolyte was zerolit C-20 for the acid and zerolit A-20 for the alkali. The film electrodes (without any supporting polymer structure) were held on each side of the matrix by the cell housing. The cell construction was similar to that described by Grubb and Niedrach (12). The electrodes studied were 3 in diameter circles. In addition some initial studies were also made concerning the polarization behavior of the oxygen electrode with free electrolyte (without any supporting matrix) using circular, thin electrodes in Cells of Type IIB.

TYPE III An H type glass cell with a fritted glass disc separator was used for studying the open-circuit behavior of various porous electrodes in conjunction with a saturated calomel or a hydrogen reference electrode. These cells, however, had relatively high internal resistance even with 30% KOH as the electrolyte and were primarily used for open-circuit and low current density behavior of the oxygen electrode with different types of catalytically active carbon electrodes. The results obtained with this type of cell must be considered only of preliminary nature.

In addition, a fairly large and concentrated effort was devoted to a rather complete review of the literature concerning the oxygen electrodes with particular reference to the fuel cell systems. A comparison of the polarization behavior of the oxygen electrode in various types of fuel cells, with a variety of catalysts investigated during this contract with the best results published in the literature was considered vital for this work.

The internal resistance of the ion exchange membrane and other cells was measured by different techniques which included (1) 60 cycle a.c. bridge made by Industrial Instruments Co. This bridge is suitable for resistances in the range of 1.0 to 0.001 ohm. (2) General Radio Impedance Bridge, Type 1650A, Serial No. 641A, 1000 cycles. Both these bridges gave almost identical results. (3) Interruptor technique using the Kordesch-Marko type circuit, (13)- described in Progress Report No. 11. In using this technique, both d.c. polarization curves (useful terminal voltage including IR losses) and a.c. polarization (d.c. terminal voltage less IR as given by the current interruption) curves were recorded. The difference in two voltages at a given current density would then give the IR drop at that current density. The value of the internal resistance obtained in this way was generally in good agreement with that obtained by other methods. In a few cases, the interruptor technique with molecular hydrogen gas on both sides of the standard ion-exchange membrane cell was used to check the behavior of the hydrogen electrode under these conditions. The current density-voltage curve generally coincided with the current density axis suggesting that the two hydrogen electrodes under these conditions were behaving nearly reversibly. In some cases, the ion-exchange membrane cells with Hydrogen gas at both electrodes were driven by an external d.c. source. With the current density range investigated, the current-density voltage plot gave a straight line passing through the origin, and the slope of the line was in good agreement with the value of the internal resistance obtained by other method. Here was a further indication that under these conditions, the two hydrogen electrodes behave apparently reversibly.

The resistance measurement obtained by the above method was compared with the slope of the linear portion of the d.c. polarization plots of the hydrogen-oxygen cells in order to get IR-free polarization plots. If it can be established beyond any doubt that the hydrogen electrode behaves reversibly at all pH values, then the polarization data reported here (after IR-correction) would represent the polarization due to the oxygen electrode.

Figure (2) represents the typical data used for calculating the internal resistance of a representative ion-exchange membrane fuel cell. The curves are self-explanatory.

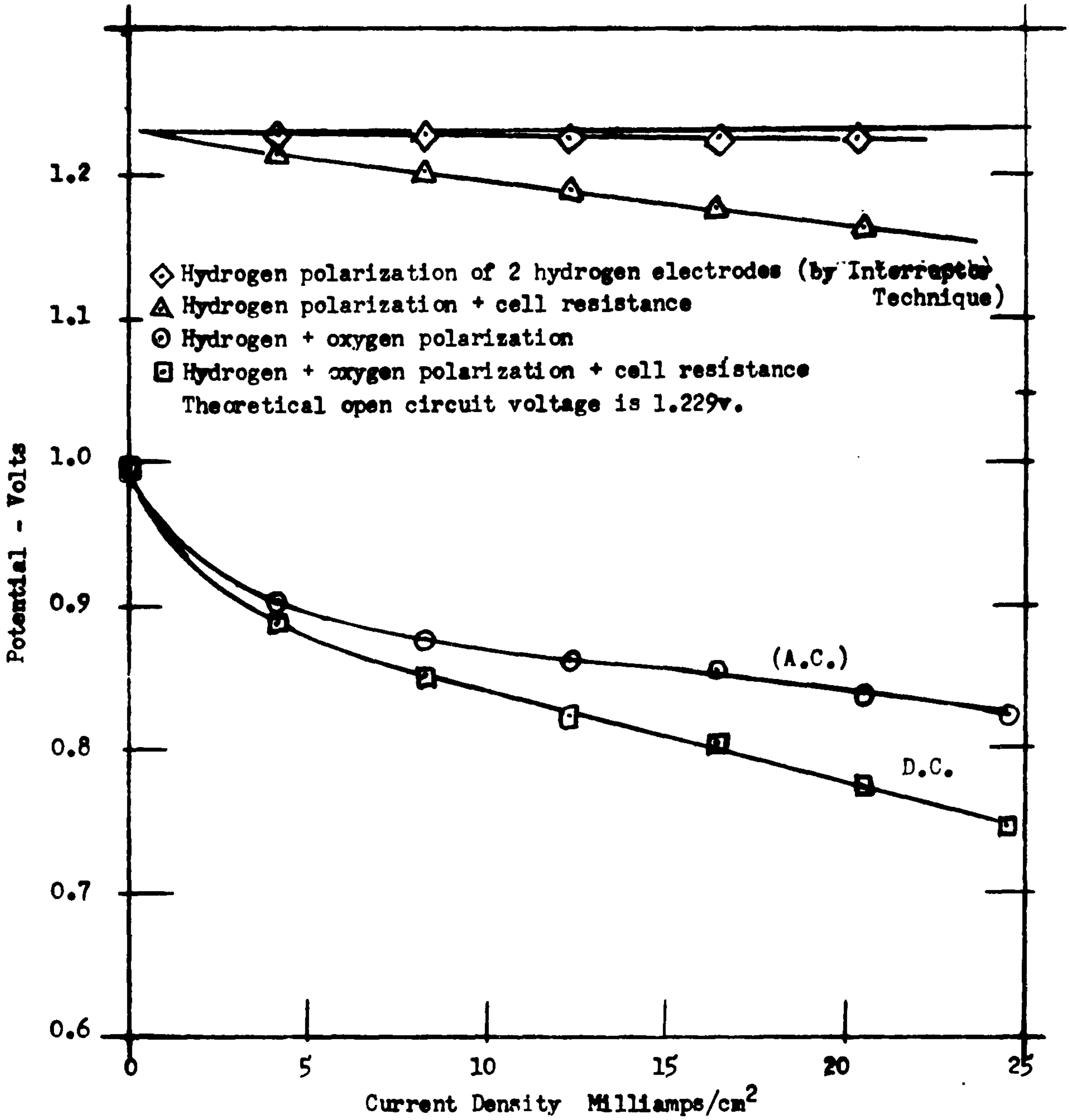


Figure 2

Hydrogen and Oxygen Electrode Polarization
and Internal Resistance (by Interruptor Technique)

3.0 Experimental Results

Initially most of the polarization data were plotted as volts versus logarithm of current density. Such plots revealed that the catalytic electrodes used for fuel cell applications do not obey the Tafel law. Some representative plots of cell emf (or electrode potential) versus logarithm of current density are given in the Appendix A. The linear plots (volts versus current density) showing an initial rapid voltage drop near the open circuit conditions and followed by a linear region extending to fairly high current densities are most instructive. It is convenient to present and discuss the linear and the non-linear sections (including the open circuit) of the polarization plots separately. The current density is based on the geometric or the apparent area.

A. Linear Polarization plots for the H_2/O_2 fuel cells

Representative polarization data for the H_2/O_2 fuel cells of the types IA, IB, IIA and IIB defined earlier are given in Figures 3 to 9 respectively. Necessary information about the cell type, the nature of the electrolyte and the method of IR corrections whenever employed is given in each figure. The catalyst used for the oxygen electrode in each of cells of Figures 3 to 9 was platinum black. The linear portion of each plot (with or without IR correction) is extrapolated to zero current density and it is seen that the extrapolated value of the voltage or emf at zero current is approximately 0.93 ± 0.02 volts.

Comparison with the Literature Value

Table 2 gives the comparison of the polarization characteristics of the various H_2/O_2 fuel cells investigated during the present contract work with some published data for the Bacon cell (14) the Justi cell (15) and the Elmore and Tanner (16) cell respectively. It may be noted that the Bacon cell data is for $200^{\circ}C$, 600 psi pressure, Justi cell data is for $80^{\circ}C$ and 2.5 Kg/cm^2 pressure, whereas Elmore and Tanner cell was operated at approximately $150^{\circ}C$. In spite of these differences in the operating temperatures and pressures, catalyst materials, the differences in the physical and chemical characteristics and pH of the electrolytes, the intercept in each case is approximately at 0.93 volts. It is particularly significant to note that increase of temperature has substantially negligible effect on the value of the voltage intercept. For the ion-exchange membrane fuel cells with platinum black catalysts, increase of temperature to about $75^{\circ}C$ was found to have substantially negligible effect on the voltage intercepts. Similar results showing that temperature has no significant effect in reducing the initial polarization loss for fuel cells using platinum black catalysts have been reported (17). It is interesting to compare these effects with similar negligible effects of temperature on the polarization characteristics of the hydrogen electrode made with platinum black (18).

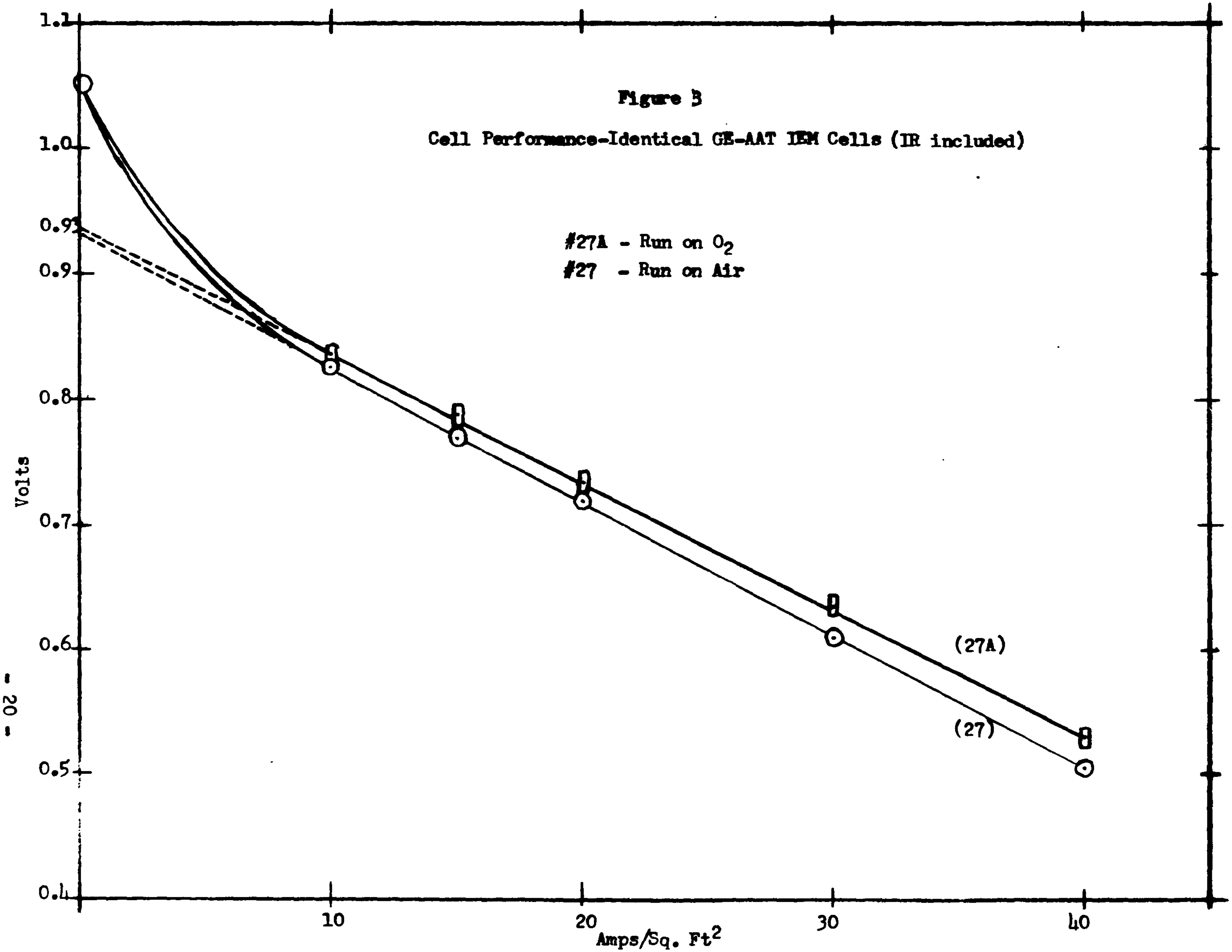


Figure 3

Cell Performance-Identical GE-AAT IEM Cells (IR included)

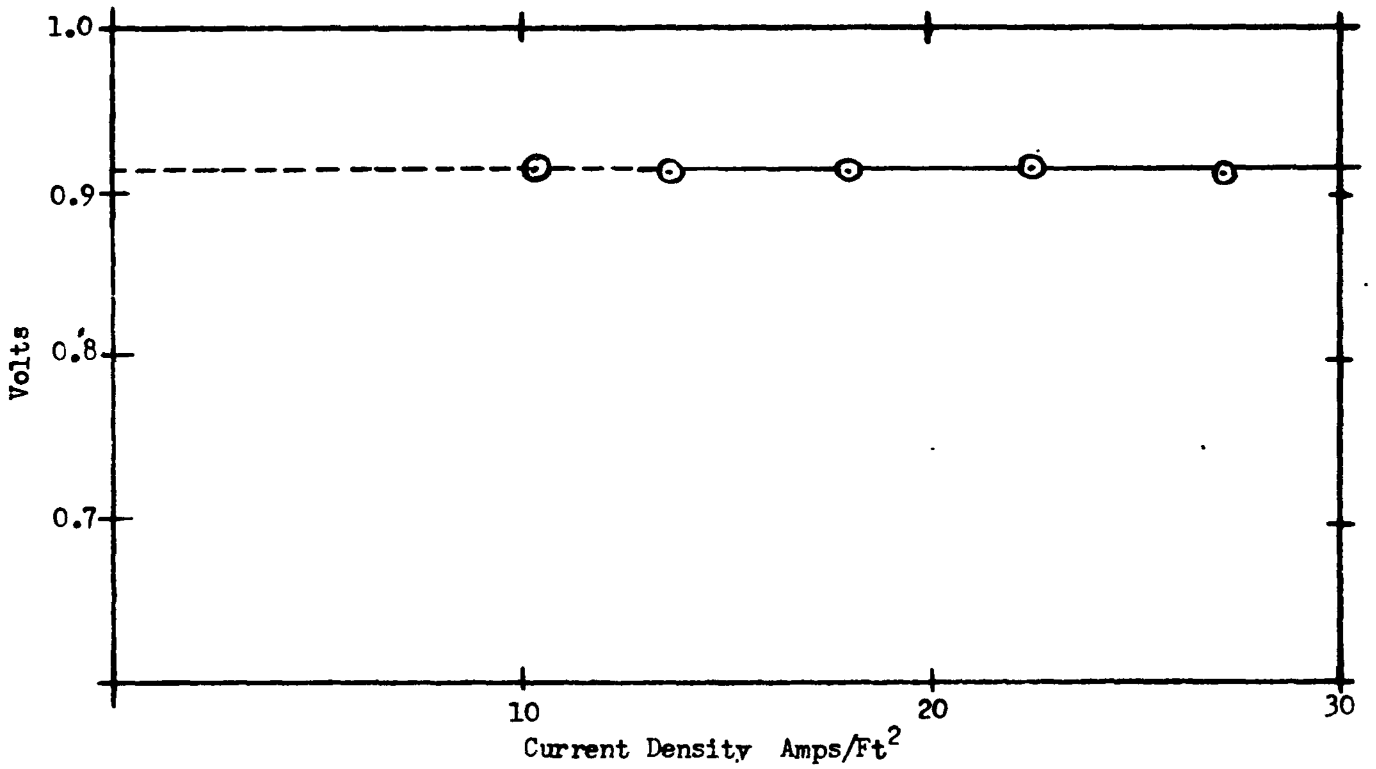


Figure 4

Typical Current - Voltage Characteristics (in absence of IR drop) of GE-AAT IEM Fuel Cell #3-A Jan. 19, 1961

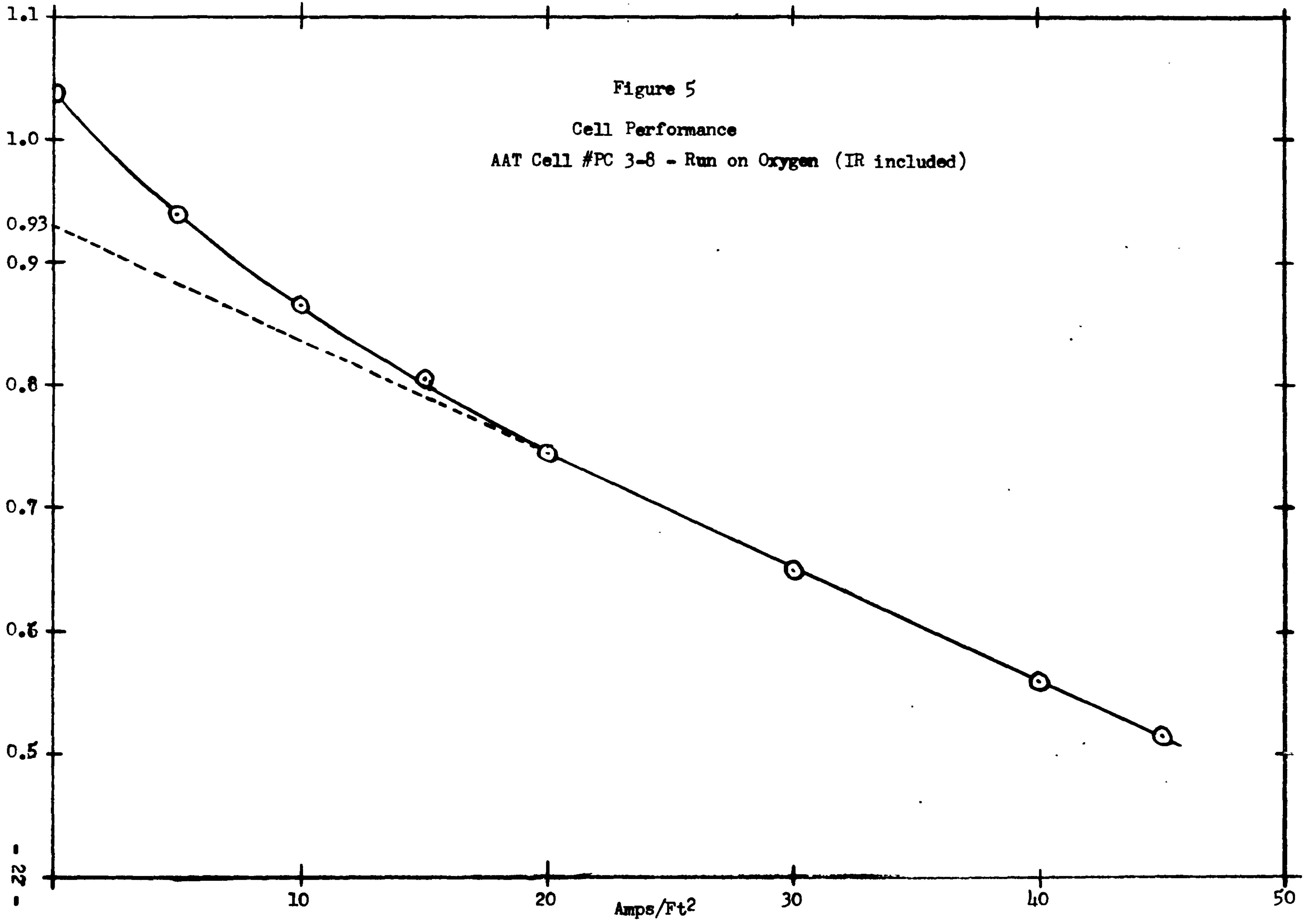


Figure 5

Cell Performance

AAT Cell #PC 3-8 - Run on Oxygen (IR included)

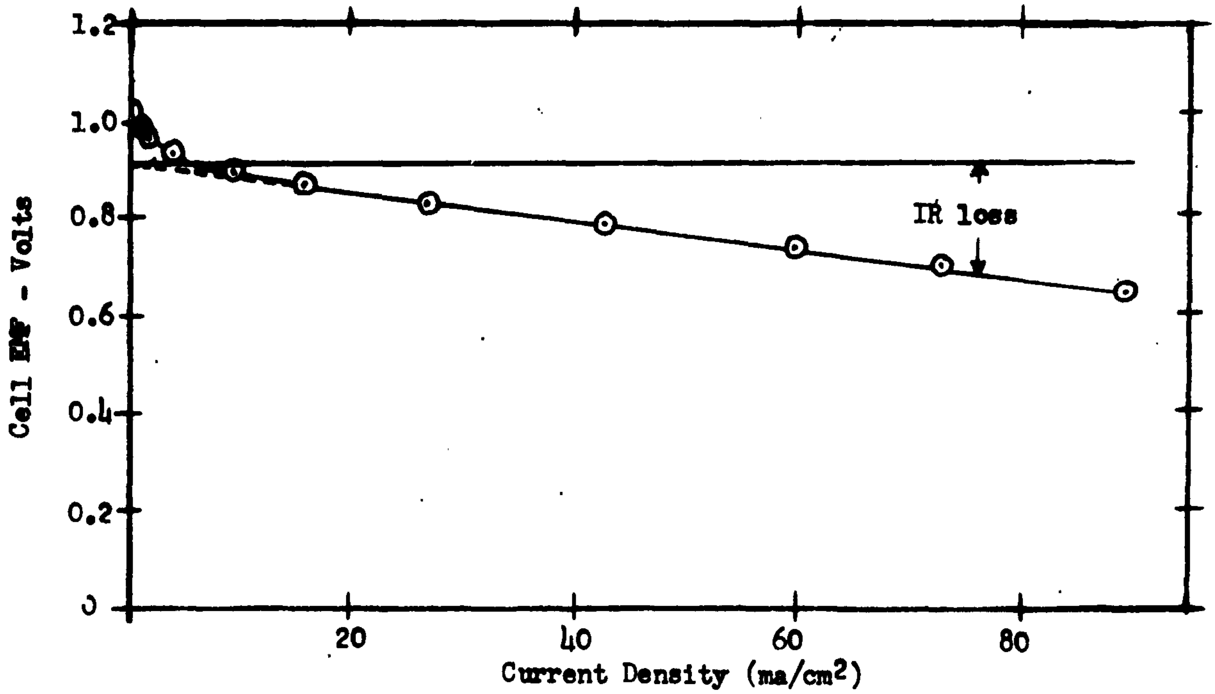


Figure 6

Performance of Cell with Pt Electrodes
Electrolyte = Zerolit C-20 Cation Exchange
Membrane After Equilibration with 2N H_2SO_4

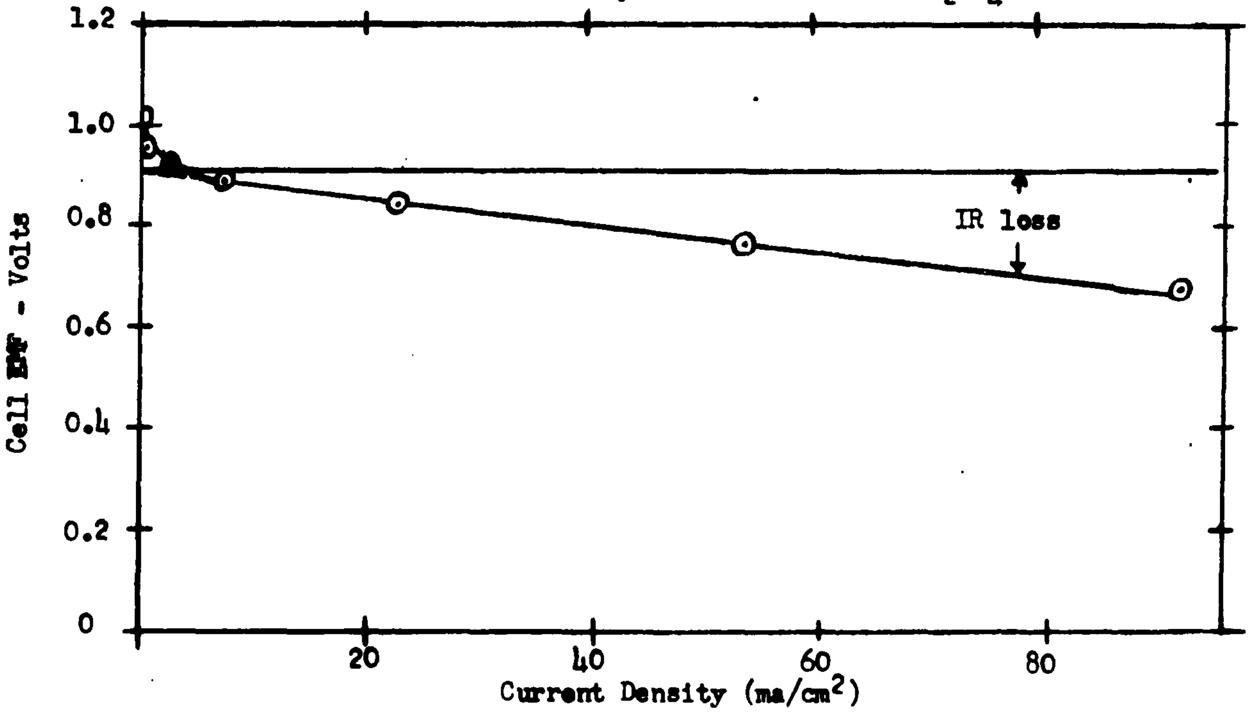


Figure 7

Performance of Cell with Pt Electrodes
Electrolyte = Zerolit A-20 Anion Exchange
Membrane after Equilibration with 30% KOH

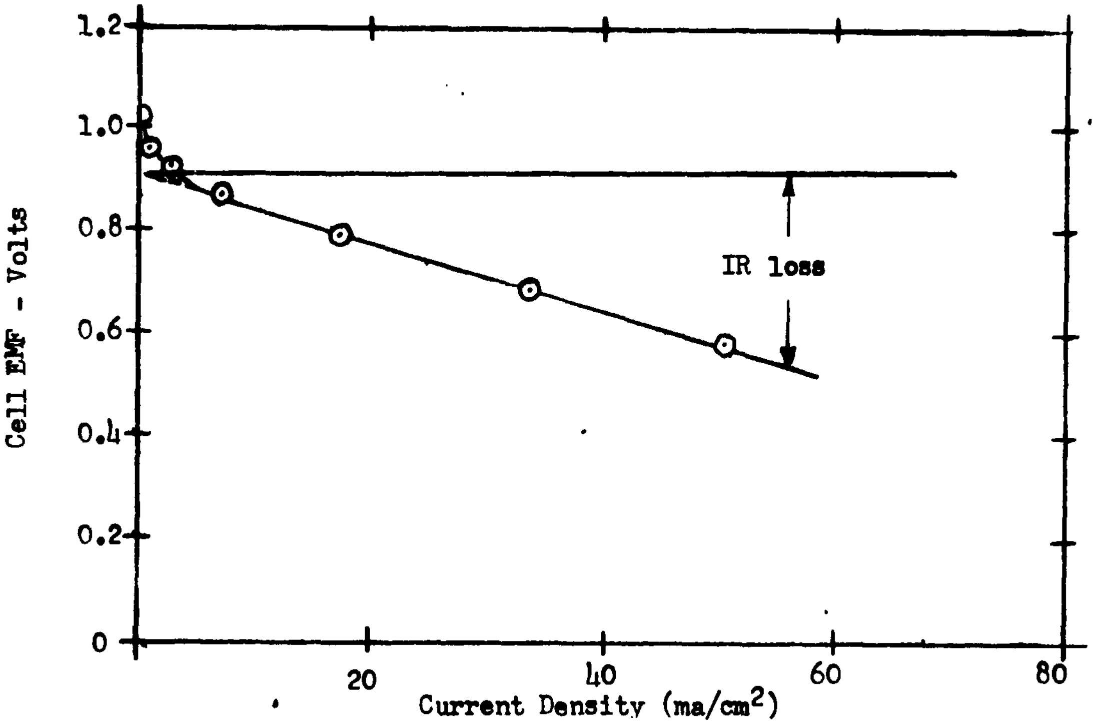


Figure 8

Performance of Cell with Pt Electrodes
Electrolyte = 2N H_2SO_4 in Dynel Matrix

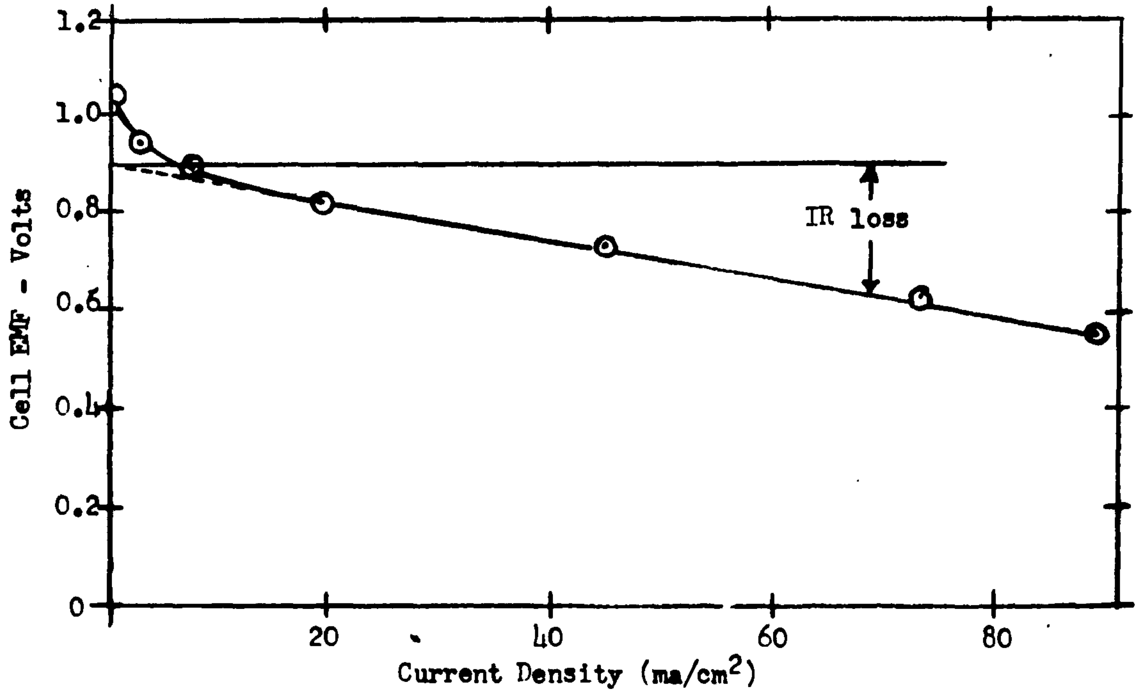


Figure 9

Performance of Cell with Pt Electrodes
Electrolyte = 30% KOH in Dynal Matrix

SUMMARY OF LINEAR POLARIZATION PLOTS FOR H_2/O_2 FUEL CELLS
COMPARISON WITH SOME PUBLISHED DATA

CELL TYPE	ELECTRODE; ELECTROLYTE TEMP; PRESSURE	VOLTAGE INTERCEPT APPROX. (EXTRAPOLATED)	LINEARITY RANGE MA/CM^2 APPROX.	SLOPE AFTER IR CORRECTIONS (REMARKS)
GENERAL ELECTRIC CELLS				
TYPE I-A	Pt BLACK, IEM 25°-$75^{\circ}C$, AIR OR O_2	0.93 ± 0.02	10 TO 75	NEGLIGIBLE
I-B	Pt BLACK, H_2SO_4, $25^{\circ}C$ AIR OR O_2	0.93	10 TO 100	CHANGES IN THE SLOPE GOVERNED PRIMARILY BY H_2SO_4 CONC. AND L
II-A	Pt BLACK, $2NH_2SO_4$, $25^{\circ}C$ 1 ATM.	0.93 ± 0.02	10 TO OVER 150	NEGLIGIBLE
II-B	Pt BLACK, 6NKOH, $25^{\circ}C$; 1 ATM.	0.93	10 TO OVER 250	NEGLIGIBLE
BACON CELL (PRIVATE COMMUNICATION)	DOUBLE POROSITY, ACTIVE Ni; 30% KOH, $\underline{200^{\circ}C}$, 600 PSI	0.94	50 TO OVER 1600	NEGLIGIBLE AS SHOWN BY RA ρL
JUSTI ET AL	DSK RANEY Ni & Ag, $80^{\circ}C$, 2.5 KG/CM^2	0.93	~UP TO 600	FINITE (IR CORRECTIONS MADE BY JUSTI ET AL)
REF: "HIGH-DRAIN HYDROGEN-DIFFUSION ELECTRODES OPERATING AT AMBIENT TEMPERATURE AND LOW PRESSURE" FRANZ STEINER, VERLAG GMBH, WIESBADEN, GERMANY, 1960. FIG. 118, CURVE C. ENGLISH TRANSLATION.				
ELMORE AND TANNER JES; 108, 669, 1961	Pd FOIL ANODE; Ag CATHODE 40% NaOH + 40% KOH + 20% $Ca(OH)_2$; $\underline{150^{\circ}C}$	0.93	30 TO 90	NOT REPORTED; WITH 35% H_3PO_4 + 65% SiO_2 O.C.V. ~ 0.8 V; ALSO $V_{ext.}$ ~ 0.75 V; $100^{\circ}C$, $125^{\circ}C$, $150^{\circ}C$.

Table 2

NOTE: PERFORMANCE DATA IN THIS AND OTHER TABLES AND FIGURES ARE FOR ILLUSTRATION ONLY IN THE DEVELOPMENT OF THE AUTHOR'S HYPOTHESIS. THEY DO NOT NECESSARILY REPRESENT PERFORMANCE DATA THAT MAY NOW BE OBTAINABLE FROM THE SYSTEMS OF THE TYPE SPECIFIED.

Effect of different catalysts for the oxygen electrode in the ion-exchange membrane cell:-

Polarization data (not corrected for IR) with different catalysts for the oxygen electrode are given in Figure 10. Cells 6, 13, 14 and 15 had only platinum black (various amounts) as catalyst whereas other cells had a variety of catalysts including, Pd, Mo, W, PtO, etc. Only with platinum black catalyst, the slope of the linear polarisation plot agreed with the resistance measured by other methods.

Polarization characteristics of cells containing carbons:

Figure 11 gives the polarization characteristics of the ion-exchange membrane fuel cells with oxygen electrodes consisting of various mixtures of carbon and platinum black specified in Table 3. The polarization curves were obtained with the interruptor technique and thus include essentially no IR drops. It may be noted that the slopes of the IR-free linear polarization plots appear to be roughly proportional to the amount of carbon present.

Effect of various methods of applying the platinum black catalyst.

These data are given in the Table 4. It is tentatively concluded that a mechanical dry mix of platinum black with carbon gives at least as good results as other methods of platinizing the carbon blacks. Because of the complexity of various parameters involved and due to the difficulties of interpreting such results, this type of work was not persued any further during the present contract work.

B. Behavior of the oxygen electrode and H_2/O_2 Fuel cells on open circuit and at low current densities:

Measured values of the emf of H_2/O_2 fuel cells or the potentials of the oxygen electrode on open-circuit and at low current densities do notconform to any of the criteria of the thermodynamic reversibility outlined under thermodynamic principles. Measured values are affected by a number of non-thermodynamic parameters including the following:-

(a) Time variation, often irregular and at present unpredictable
(b) Type of electrode material e.g. Pt, Pd, C
(c) Surface area and activity e.g. bright Pt versus platinum black
(d) Electrolyte pH
(e) Stirring or agitation
(f) Presence of foreign ions e.g. chloride, bromide, iodide ions
(g) Pre-electrolysis of electrolytes
(h) Electrode Geometry, cell design, position and construction of the reference electrodes etc.

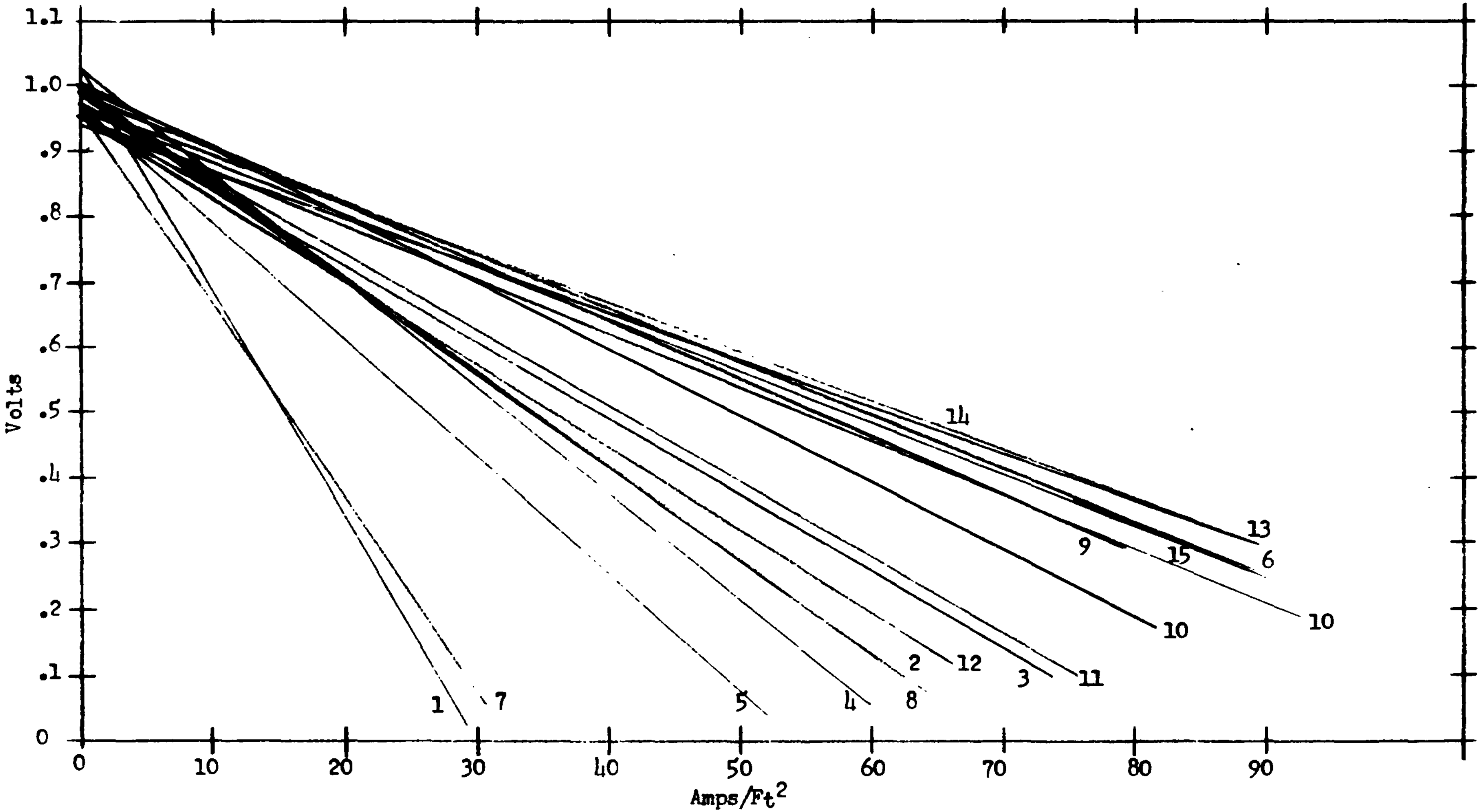


Figure 10

Polarization Characteristics of H_2/O_2 Fuel Cells (IR included)
Constant Electrolyte (GE IEM, Type IA)
Different Catalysts for the O_2 Electrode
(Current Collector Set #1)

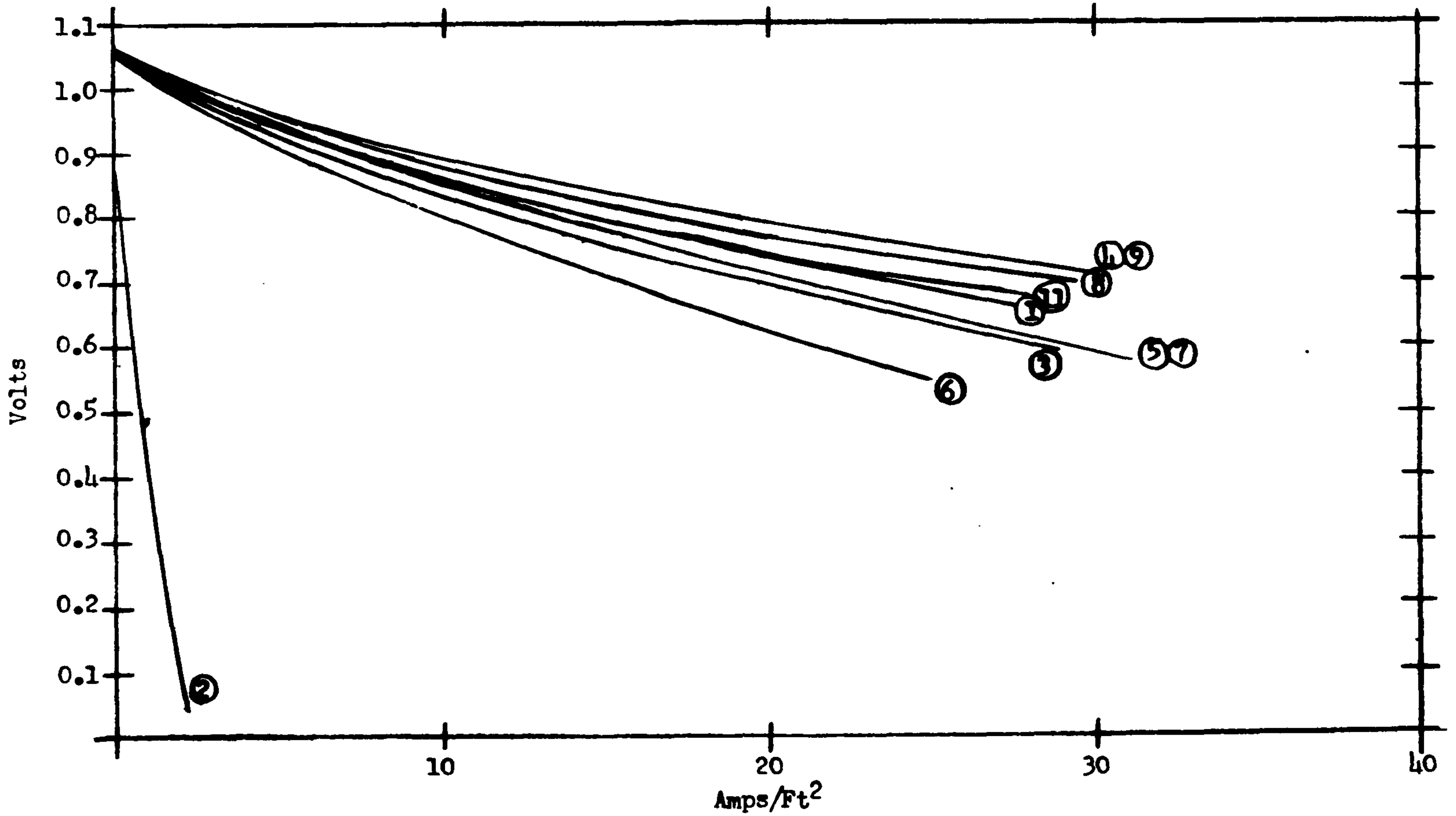


Figure 11

Performance of 4" x 4" IEM Cells with Different Amounts of Carbon and Platinum

For explanation see Table

TABLE 3

Data concerning the relative amounts of carbon to platinum used for the oxygen electrode for ion exchange fuel cells.

All cells are 4" x 4" acidic ion-exchange membrane cells with 3 ply reinforcement.

Catalyst loading on the fuel (H_2) side is constant at 0.0375 g palladium per square inch.

LOADING FOR THE OXYGEN SIDE (DRY MIXTURE)

Cell #	Carbon g/in^2	Platinum g/in^2
SC-1	0.016	0.0187
SC-2	0.021	none
SC-3	0.010	0.0375
SC-4	0.010	0.0187
SC-5	0.0045	0.0187
SC-6	0.021	0.0187
SC-7	0.007	0.0187
SC-8	none	0.075
SC-9	0.006	0.056
SC-11	none	0.1125

TABLE 4

Performance of the Ion Exchange Membrane Fuel Cell as a Function of the Oxygen Electrode

Cell Dimension: 4" x 4" active area; 0.025" thick; Webril reinforced; sulfonated phenol-formaldehyde polymer membrane.

Fuel (hydrogen) electrode constant in all cases (0.037 g. Pd/in^2).

Cell #	O_2 Electrode Composition grams/in^2			A.C. Resistance ohms	Open Circuit Voltage	Current Density in Amp/ft^2 at Useful Termined Voltage				Remarks
	Pt	Pd	C			.08 V	0.7 V	0.6 V	0.5V	
12	.02		.02	0.034	1.04	9.0	14.4	22.1	30.6	
13	.01		.02	0.042						Not tested
14	.005		.02	0.089						Not tested
15A	.01		.03	0.060	1.04	7.2	10.8	16.7	24.1	
17	.01		.02	0.034	1.03	10.8	16.4	24.3	34.2	(3)
18	.01		.02	0.038	1.00	10.6	17.8	28.8		
19			.0375	0.053	0.98	9.0	13.1	18.9	24.8	(1)
20			.0375		0.97					(2) Low Performance
22	.1125			0.029	1.06	14.9	25.2			
23	.015		.020							Not tested
24	.02		.015	0.034	1.02	8.8	13.5	18.9	24.8	
25	.03		.015	0.029	1.07	14.0	19.8	26.5		
26	.02		.01	0.030	1.03					Data unreliable
27	.03		.01	0.029	1.07	15.3	21.6	29.7		

TABLE 4 (Cont'd)

Cell #	O_2 Electrode Composition grams/in^2			A.C. Resistance ohms	Open Circuit Voltage	Current Density in Amp/ft^2 at Useful Termined Voltage				Remarks
	Pt	Pd	C			.08V	0.7 V	0.6 V	0.5 V	
28			.03							(5) Not tested
29	.03		.006	0.028	1.02	9.7	17.6			
30	.02		.006	0.034	1.03	10.4	18.9			
33	.01	.03		0.027	1.00	10.6	18.0			
34	.02		.005	0.033	1.04	12.6	19.8	27.5		(6)
35	.02		.005	0.034	1.02					Not tested (400 mesh C)
36	.015		.005	0.036	1.02		15.3	20.7	25.7	(400 mesh C)
37	.02		.007	0.034	1.046	9.0	18.9	28.8		
38	.03		.007	0.028	1.06	14.4	24.7	34.7		
39	.03		.003	0.030	1.03		21.2	31.5		
40	.02	.0375	.005	0.030	1.02	10.8	21.3	31.5		
41	.02	[illegible]	.005	.030	1.02	11.7	22.1	32.4		
42	.02	(.005, 20%D)								*Not tested
43	(.005, 20%D)									*Very poor performance
44	.025		.007							Not tested

*Darco carbon treated with 20% pt.
Special carbons prepared by Dr. H.J. Maget
(1) Particle size 5-10 microns (platinized carbon)
(2) Particle size 20-40 microns (platinized carbon)
(3) Particle size 5-10 microns
(5) Particle size 5-10 microns (platinized carbon)
(6) Particle size less than 5 microns

(j) Reported effects of superimposed a.c. on the d.c.

In addition, two important and rather unusual observations concerning the open circuit voltage of the oxygen electrode are:

(1) Time-dependent open circuit voltages greater than the theoretical maximum of 1.23V at room temperature under certain conditions.
(2) Experimentally observed effects of higher temperatures (fused electrolytes) which at present cannot be explained by the classical thermodynamics.

A brief summary of these results is reported below:

Variation with time:

The time-variation of the O.C.V. of the oxygen electrode, observed by practically all the investigators studying the oxygen electrode, presents the single most troublesome variable in the study of the oxygen electrode on O.C.V. and at low current densities. However, this factor has been ignored by a majority of investigators and this contributes to the serious lack of agreement in the results obtained by different investigators. Apparently, this effect has not yet been systematically investigated under controlled conditions designed to minimize the effect of other variables.

It is generally observed that for a given electrode material, the time variation is least with catalytically active or rough surfaces compared to smooth, bright surfaces, and that in aqueous alkaline media, the time variation is relatively small compared to aqueous acidic media. One rather remarkable observation is that with the ion-exchange membrane fuel cells, the open-circuit voltage of the oxygen electrode with platinum black is established relatively rapidly (in about 5 minutes) and this value shows little or no change as a function of time over several hours or days.

Some time variations of the O.C.V. are given in Table 5 and in Figures 12, 13 and 14. Additional data are given in Tables 8 and 9.

(b) Effect of the type of electrode material:

Table 6 gives data for the O.C.V. of a large number of ion-exchange membrane H_2/O_2 fuel cells made with different catalysts for the oxygen electrode. Replacing palladium black for the platinum black for the hydrogen electrode with constant oxygen electrode showed no significant change in the O.C.V.

Data published in the literature refer primarily to platinum black, bright platinum, and carbon electrodes for aqueous acidic systems and these plus nickel and silver for the aqueous alkaline electrolytes.

Table 5

Oxygen Electrode Potential

Open Circuit Voltage as a Function of Time

Time (min.)	Potential	Time (min.)	Potential	Time (min.)	Potential
0+	0.420 (1)	225	1.139	428	1.177
2	0.475	227	1.165	438	1.190
5	0.512	236	1.198	448	1.199
9	0.630	238	1.203	458	1.206
12	0.825	246	1.219	473	1.213
15	0.908	249	1.226	488	1.219
22	1.026	252	1.227	496	1.222
24	1.045	255	1.231	513	1.227
27	1.110	260	1.235	553	1.233
30	1.154	273	1.243	580	1.238
33	1.184	279	1.246	585	1.238
36	1.204	284	1.248	588	1.238
41	1.238	290	1.251	602	1.241
42	1.220 (4)	303	shorted out	618	1.241
|	1.225 (4)	304	1.010	| (1)	- (2)
|	1.234 (4)	306	1.085	619	1.230
|	1.237	307	1.091 (3)	623	1.235
47	1.238 (5)	313	1.093	636	1.239
48	1.242	shut down overnight		654	1.238
85	1.228	313 +	0.217 (1)	658	1.240
108	1.216	326	0.343	671	1.243
112	1.214	334	0.491	698	1.246
124	1.178	336	0.647	708	1.248
126	1.178	341	0.837	718	1.250
127	1.190 (2)	346	0.915		
131	1.218	354	1.037		
135	1.190	357	1.064		
136	1.203	362	1.090		
143	1.225	365	1.093		
145	1.225	369	1.097 (2)		

Table 5 (Cont'd)

Time (min)	Potential	Time (min)	Potential	Time (min.)	Potential
147	1.228	373	1.108		
150	1.224	375	1.115		
165	1.162 (1)	380	1.128		
175	1.145	385	1.138		
198	1.132	390	1.144		
212	1.116	409	1.159		
219	1.122 (2)	418	1.165		

(1) O_2 electrode fully immersed

(2) O_2 electrode 1/4 immersed

(3) O_2 electrode 1/2 immersed

(4) Using different Rubicon potentiometer

(5) Readings taken using both potentiometers

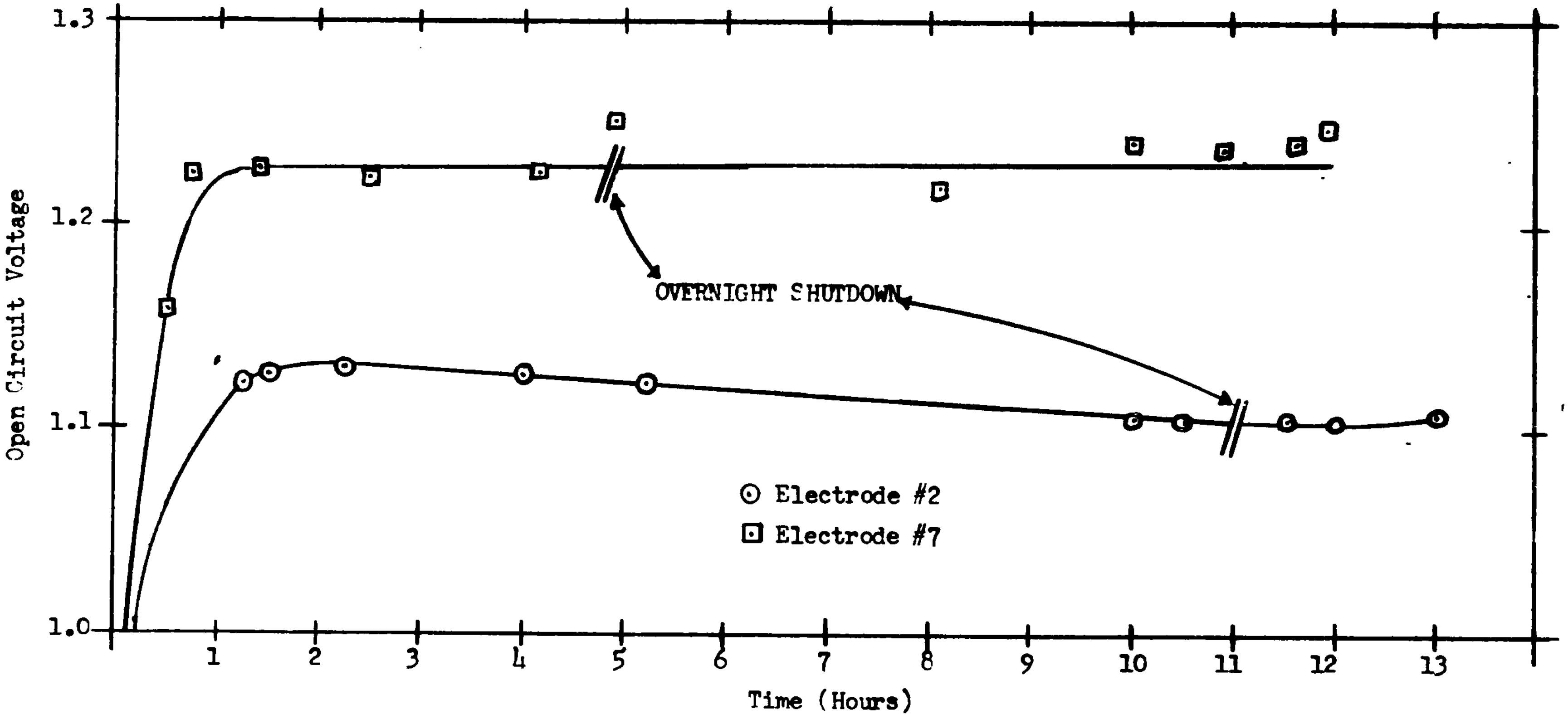


Figure 12

Open Circuit Voltage of the Oxygen Electrode Versus Reversible Hydrogen Electrode in the Same Solution; Platinized, Wet Proofed Carbon in 25% KOH

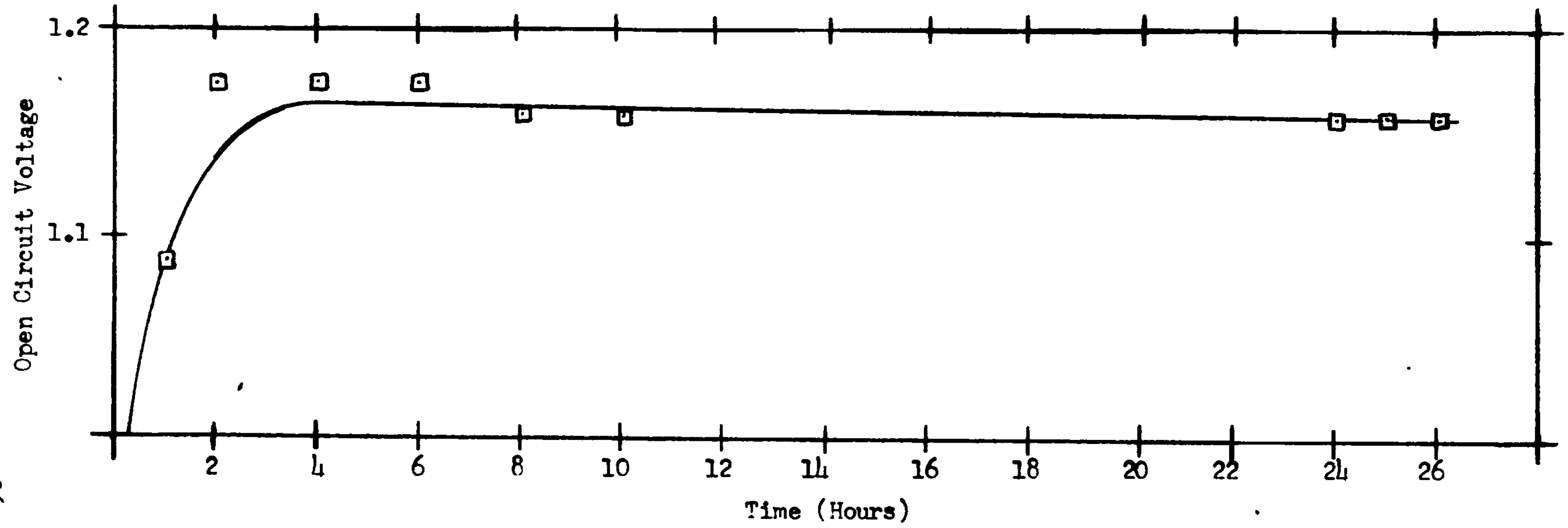


Figure 13

Open Circuit Voltage of the Oxygen Electrode Versus Hydrogen Electrode in the Same Solution; 25% KOH. Both Electrodes Platinized Platinum Screen.

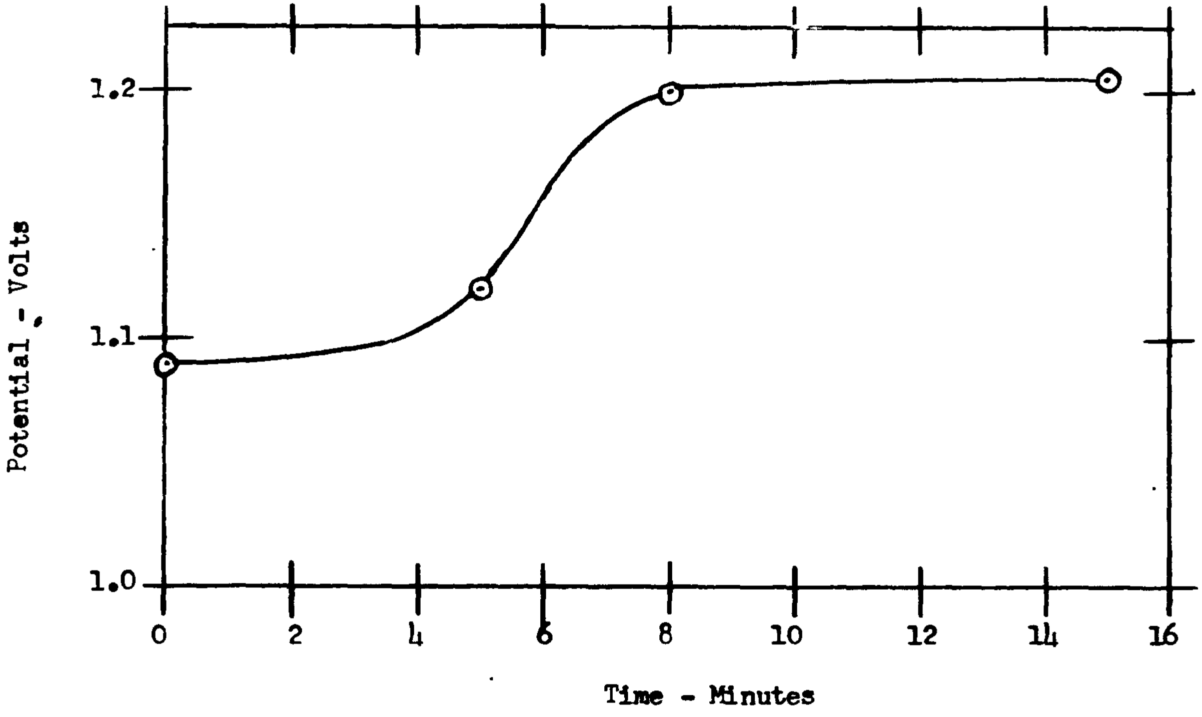


Figure 14

Open Circuit Voltage Versus Time for Platinized Stackpole Grade 219xG Carbon Oxygen Electrode Wetproofed with Teflon.
Referred to Platinized Platinum Hydrogen Electrode in the Same Solution.

Table 8

Effect of different catalysts on oxygen depolarized carbon electrodes in an alkaline system: **Electrode type:**
Stackpole Carbon 219 x G; 5/8" dia., 1" long. **Method of activation:** 800°C for 5 minutes; quenched in distilled water, dried at 800°C for 3 minutes.

Catalyst application: Treatment with respective nitrates, (except for platinum which was deposited from Chloroplatinic acid) followed by decomposition at 200°C for 2 hours.

Wet Proofing: 30% teflon suspension, dried at 150°C for 16 hours.

Electrolyte: 25% KOH

Catalyst	Current Drain Milliamperes	Cell Voltage (H_2 Reference)	Time (Mins. After Start of Run	Remarks
None	0.0	1.02	15	
	2.0	0.975	20	
	20.0	0.480	--	
Platinum Black	0.00	1.09	0	Readings check using two different potentiometers and rechecked the standard cell against a certified standard cell. Experiment successfully repeated using another "219xG" carbon.
	0.00	1.12	5	
	0.00	1.20	7	
	0.00	1.207	15	
	3.00	1.006		
	10 .0	0.750		
Cobalt	0.00	0.992	about 1 hr.	
	2.00	0.950		
	10.00	0.747		

Table 8 (Cont'd)

Catalyst	Current Drain Milliamperes	Cell Voltage	Time (Mins.)	Remarks
Iron	0.00	1.05		Potential rose above 1.06 immediately on test and then dropped.
	2.00	0.994		
	5.00	0.890		
Copper	0.0	1.078	15 mins.	
	2.0	1.00		
	10.00	0.46		
Chromium	0.00	1.105		
	2.00	1.053		
	5.00	0.940		Potential falling to 0.810 in 25 minutes.
Aluminum	0.00	0.930		
	2.00	0.793		
	5.00	0.721		
Nickel	0.00	1.055	2	Falling as a function of time.
	2.00	0.983		
	5.00	0.797		

Table 9

Effect of different catalysts on oxygen depolarized carbon electrodes in an acid system:
For details concerning the electrode preparation see Table 8
Electrolyte: Sodum Acetate Acetic Acid Buffer, pH of 4.0.

Catalyst	Current Drain Milliampere	Cell Voltage (Vs H_2 reference)	Time in Minutes after Start of Run	Remarks
No catalyst	0 0.20 0.77	0.855 0.635 0.051	15 mins.	One repeat run with same results; 0.870V open circuit.
Platinum	0 0.20 0.780	0.8634 0.6193-0.667 0.052	10 mins.	0.88V. at 0.0 Ma in a repeat run about the same polarization.
Iron	0 .20 0.725	0.860 0.620 0.048	10 mins.	
Aluminum	0 0.20 0.55	0.80 0.49 0.037	20 mins.	
Nickel	0 0.20 0.75	0.763 0.570 0.050	15 mins.	
Copper	0 0.20 0.70	0.778 0.570 0.046	after 6 mins.	

Table 9 (Cont'd)

Catalyst	Current Drain	Cell Voltage	Time in Min.	Remarks
Chromium	0	0.848	2 mins.	
	0.20	0.570		
	0.40	0.035		
Cobalt	0	0.830	0	
	0.20	0.653		
	0.87	0.058		

Table 6

OPEN CIRCUIT VOLTAGES OF THE G.E. CATION EXCHANGE MEMBRANE, HYDROGEN-OXYGEN FUEL CELLS AS A FUNCTION OF THE "CATALYTIC" ELECTRODE MATERIAL. CELL THICKNESS ABOUT 0.025 INCHES. ROOM TEMPERATURE. (PLATINUM & PALLADIUM BLACKS AS RECEIVED FROM ENGLEHARD IND. UNLESS OTHERWISE STATED).

Hydrogen Electrode	Oxygen Electrode	Steady State OCV (volts)	No. of Cell Studies	Cell Sizes (area in sq. inches)	Remarks
Platinum	Pt black	1.065 ± 0.005	Hundreds	1.8, 16, 83, 100	Excellent reproducibility and repeatibility
Palladium	Pt black	1.065 ± 0.005	Hundreds	1.8, 16, 83, 100	Same as above
Platinum	Pd black	0.96 ± 0.01	Several dozen	1.8, 16, 100	Same as above
Palladium	Pd black	0.96 ± 0.01	Several dozen	1.8, 16, 100	Same as above
Palladium	Pd/Pt blk, mixtures	0.98 - 1.03	Approx. 6	16, 83	O.C.V. depends on relative amts of Pt & Pd in mixture
Palladium	Rhodium black	0.92 ± 0.03	3	1.8	Reproducibility poor - varies irregularly with time
Platinum	Rhodium black	0.92 ± 0.03	2	1.8	Same as above
Palladium	Iridium black	0.95 - 0.88	3	1.8	Poor reproducibility
Platinum	Ruthenium black	0.82	1	1.8	No remark
Palladium	Ruthenium black	0.82	1	1.8	Same as above
Palladium	Stackpole carbon platinized with $H_2Pt\ Cl_6$	0.87	1	16	Same as above
Palladium	Stackpole carbon platinized with colloidal Pt	0.775	1	16	Same as above
Palladium	Pt blk on battery carbon	0.97	1	16	Same as above
Palladium	Pt blk on coke	1.03	1	16	Same as above
Palladium	Pt blk on acetylene carbon blk.	0.98	1	16	Same as above

Table 6 (Cont'd)

Hydrogen Electrode	Oxygen Electrode	Steady State OCV (volts)	No. of Cell Studies	Cell Sizes (area in sq. inches)	Remarks
Palladium	10% Pd on Shawinigan carbon blk.	0.98	1	16	Same as above
Palladium	Titanium carbide platinized with Chloroplatinate	0.775	1	16	Same as above
Palladium	Tungsten Carbide platinized with Ammonium Chloroplatinate	0.867	1	16	Same as above

A significant observation concerning the effect of pH is that platinum black, active nickel, active silver and catalyzed carbons in alkaline electrolytes (6N NaOH or KOH) give approximately 1.1 to 1.15 volts for the open circuit potential of the oxygen electrode with respect to a hydrogen electrode in the same solution under otherwise apparently identical conditions.

A summary of the comparion of the data on O.C.V. obtained during the present contract work with some typical published data is presented in Table 7.

(c) Effect of surface area and activity:

Tables 4, 6 and 7 summarize the effect of these variables. It is generally observed that bright, smooth electrodes in general give lower, and irreproducible results. This apparently can be attributed to the differences in surface area and activity. Additional data are given in Tables 8 and 9 together with pH effects.

With liquid electrolytes, the total surface area under the electrolyte also appears to have significant effect on the behavior of the O.C.V. According to Richards (19) the immersed surface of the platinum electrode must be maintained as constant as possible, "a sudden large increase of immersed surface causing a sudden fall in potential." Similar qualitative observations were repeatedly made during this work. Some data on the open-circuit voltage given in Table 5 show this effect. Similar observations with reversible hydrogen electrode behavior is reported and the area under the electrolyte is usually specified.

The effect of the method of electrode preparation, particularly of applying Platinum black has been given in Tables 4 and 6.

Surface area and activity represent the single most important variable for a fuel cell system using a given electrolyte as is evident from the large emphasis given to the catalyst preparations by different organizations. This area represents more of an art or a matter of experience rather than a science and no generalization can be made at present. It does appear however, that chemical precipitation of the catalyst on the substrate usually gives a more active and more reproducible electrode than electro - plating methods. Platinum black supplies by different suppliers usually give different polarization behavior. This maybe due, at least in part, to the differences in the specific surface areas.

It appears that a material which is a superior catalyst for the peroxide decomposition is not necessarily superior for the cathodic reduction of O_2 to OH^-. This conclusion was also arrived at independently by Hauel (20) who showed that ruthenium black, which is superior to platinum black for the peroxide decomposition is inferior to platinum black for oxygen electrode.

TABLE 7

SUMMARY OF TYPICAL SIGNIFICANT PUBLISHED DATA ON O.C.V. OF O_2 ELECTRODES OR H_2/O_2 FUEL CELLS

AUTHOR OR ORGANIZATION	O_2 ELECTRODE MATERIAL	ELECTROLYTE (APPROX.CONC)	O. C.V. VOLTS APPROX.	OTHER DETAILS REMARKS
BACON	LITHIATED NI.	30% KOH	1.1 – 1.12	200°C, 600 PSI
JUSTI ET AL	DSK RANEY AG.	6 N KOH	1.1	85°C
UNION CARBIDE	CAT. CARBONS	6 N KOH	1.1 - 1.13	25 - 60°C
GENERAL ELECTRIC CO. RES LAB. & AAT FUEL CELL LAB.	PT. BLACK	6N KOH	1.1 – 1.15	
	PD BLACK	6N KOH	1.1	
	AG, NI	6N KOH	1.1	
	PLATINIZED C.	6N KOH	1.13	HIGHER UP TO 1.24V AFTER TREATED WITH TEFLON SUSP
	PT BLACK	1.E M (pH~3.5)	1.065	HIGHLY REPRODUCIBLE
	PD BLACK	1 E M "	0.97	"
	OTHER NOBLE METALS	1 E M "	0.85 TO 1	DEPENDS ON SURF AREA AND ACTIVITY
	CAT CARBONS	1 E M "	0.95 TO 1.07	"
	PT BLACK	1-0.1 N H_2SO_4	1.0 TO 1.07	SOME FLUCTUATION DEPENDING ON THE METHOD OF PREPARATION
	PT BLACK	HAC-NAAC BUFFER ; pH=4	0.95 TO 1.07	"
	BRIGHT PT	1.0-0.1 N H_2SO_4	0.6-0.85	IRREPRODUCIBLE
	BRIGHT PT	BUFFER, pH=4	0.6 – 0.7	"
	CATALYSED C	0.1-1.0 N H_2SO_4 OR BUFFERED pH	~ 0.85	DIFFERENT CATALYSTS (EXCEPT PT) SEEM TO MAKE LITTLE DIFF
HOAR (1933)	BRIGHT PT	0.1 N NAOH	0.99	
	PT BLACK	0.1 N NAOH	1.06	
	BRIGHT PT	0.1 N H_2SO_4	0.83	
		N/15 PHOSPHATE BUFFER	0.93	
	BRIGHT GOLD	0.1 N NAOH	1.1	
BARNARTT (1959)	BRIGHT GOLD	0.1 N H_2SO_4	0.83	
	" "	"	1.46 - 1.36	AFTER ANODIC PRE-ELECTROLYSIS
BOCKRIS & HUQ (1956)	BRIGHT PT	0.01 N H_2SO_4	1 TO 0.6	IRREGULAR VARIATION.
		0.01 N H_2SO_4	0.84	AFTER CATHODIC PRE-ELECTROLYSIS
			1.24	FIRST CATHODIC THEN ANODIC PRE-ELECTROLYSIS

AUTHOR	ELECTRODE MATERIAL	ELECTROLYTE	O.C.V VOLTS APPROX.
SMALE (1894)	PLATINIZED PT.	1 N TO 10^{-3}N H_2SO_4	1.07
		1 N TO 10^{-3}N H_3PO_4	1.07
		1 N TO 10^{-3}N $CH_2CL \cdot COOH$	1.07
		1 N TO 10^{-3}N NA_2SO_4 OR K_2SO_4	1.07
		1 N TO 10^{-3}N KOH	1.1
		1 N TO 10^{-3}N NAOH	1.09
		1 N HAC	0.95
		5 N HCL	0.7
		1 N HCL	0.88
		0.1 N HBR	0.77
		0.1 N HI	0.59
RICHARDS (1928)	PLATINIZED PT.	0.5 N H_3BO_3 AMONG OTHERS	1.1
WILSMORE (1900)	PLATINIZED PT.	1 N H_2SO_4	1.07
		AFTER 4 DAYS; O.C.V. ROSE TO	1.12
		1 N NAOH	1.12
BRITTON (1925)	PLATINIZED PT.	MALONIC ACID pH = 2.28	1.195-1.228
	"	TARTARIC ACID pH = 2.29	0.82
	"	OXALIC ACID pH = 1.65	0.83

THE NOTE ON TABLE 2, PAGE 25 APPLIES TO THE ABOVE TABLE 7.

(d) Effect of electrolyte pH.

A summary of data is given in Table 7. The data for variously catalysed carbon electrodes as a function of pH are given in Tables 8 and 9. With these carbon electrodes it is generally observed that the over-all open circuit voltage for the H_2/O_2 cell in sulfuric acid solution is only about 0.82 - 0.84 volts whereas for the same electrodes in an alkaline solution, the open circuit voltage is about 1.10 V or above. It may be stated as a general observation from studies at the General Electric Company that for platinum black electrodes, the cell voltage with an ion-exchange membrane cell (pH = 3.5) is about 1.07 V; with liquid acidic electrolyte, about 1.02 V, and with liquid alkaline electrolyte about 1.10 V. With palladium black for the oxygen electrode in the ion-exchange membrane cells (pH 3.5) the open circuit voltage is about 0.97 V, whereas for the same electrode in alkaline solution, the open circuit voltage is about 1.10 V.

Rather extensive data for the pH effect have been obtained by Smale (21) and representative values were reported in the Progress Report No. 17. His results show that the potential of the oxygen electrode becomes less positive as the pH increases, but not in accordance with the Nernst equation.

(e) Effect of Stirring and agitation:

The effect is observed with practically all liquid electrolytes, though the effect is apparently more pronounced with liquid acid electrolytes. Bain's data (22) summarized in the preceding progress report are the most extensive though no general trend is as yet discernible. No satisfactory interpretation is given for this "motor Electrolytic potential."

(f) Effect of Foreign Ions:-

Foreign ions such as chloride, bromide and iodide ions appear to be preferentially adsorbed and thus lower the observed O.C.V. The work was carried in connection with another project aimed at studying the effect of various poisons (from solutions). This effect is more pronounced on the oxygen electrode as compared to hydrogen electrode. The "sorption" is essentially reversible in the sense that by prolonged treatment with distilled water, the original polarization characteristics are substantially restored.

Similar lowering of the O.C.V. of the oxygen electrode has been reported by Smale (21). Mond and Langer (22) also reported a similar effect of chloride ion. Implications in using chloroplatinic acid or chloride containing electrolytes are obvious.

(g) Effect of pre-electrolysis of solution:

Bockris and co-workers (23) are the only ones using this technique which reportedly gives "ultra pure" solutions.

In general they observed that cathodic pre-electrolysis alone gives only about 0.84V whereas prolonged anodic pre-electrolysis after cathodic pre-electrolysis gives higher open circuit voltages of about 1.24V. A different and perhaps more satisfactory interpretation of these effects is suggested later.

(h) Effect of electrode geometry and cell design parameters.

These variables are apparently neglected by the majority of workers though Barnartt (24) has initiated an extensive study of these parameters and has reported the effect of geometry, non-uniform current distribution, capillary shielding and IR drop corrections among other factors. Additional parameters which have not been apparently investigated include the method of separating the anolyte and the catholyte, the relative sizes and shapes of the counter electrodes, the nature of the electrolyte and the effect of current-interruption.

(j) Effect of high frequency a.c. and other variables.

No systematic investigation of the effect of high frequency a.c. on the oxygen electrode potential has been carried out, though it is generally known that a.c. reduces the polarization. Mantell (25) who has discussed this effect in detail concludes that "since the exact cause of overvoltage is not well understood and since methods of properly measuring it are in some respects doubtful, it is obvious that it would be difficult to make similar measurements with combined a.c. and d.c. Some literature has reported negative overvoltages under such circumstances, which at once open the question as to the suitability of the method employed." This also raises the question of the validity of various a.c. methods of current interruption used in measuring the ohmic polarization. One earlier observation by Bennewitz (26) to the effect that when the anode of an electrolytic cell is connected with the antenna of a Hertzian oscillator, the arrest in the current voltage curve occurs just above 1.23 volts, that is, just above the theoretical reversible potential is very interesting and significant.

Other factors such as water-repellant treatment of the electrode also seem to affect the open-circuit voltage behavior. Thus, treatment with certain organic hydropholic materials apparently increase the open-circuit voltage.

Because of the complexity and interdependence of these variables, progress in our understanding of the oxygen electrode on open circuit and in the non-linear region of the polarization behavior has been rather limited.

4.0 Open Circuit Voltages Greater Than the Theoretical Values:

a. At Ambient Temperatures:

Table 10 gives a summary of these observations by different investigators.

SUMMARY OF OBSERVED OPEN CIRCUIT OXYGEN ELECTRODE POTENTIALS HIGHER THAN THE THERMODYNAMICALLY CALCULATED VALUES AT LOW TEMPERATURES

TABLE 10

LOW TEMPERATURE, AQUEOUS ELECTROLYTES, O_2 ELECTRODE O.C.V.(TIME-DEPENDENT)				
AUTHORS	ELECTRODE MATERIAL	ELECTROLYTE	EXP'L O.C.V. VOLTS	OTHER DETAILS & REMARKS
W.T.RICHARDS 1928	PT. BLACK (PLATINIZED)	BORATE OR PHOSPHATE	~1.5	ALTERNATELY MADE ANODE & CATHODE TO REMOVE ANY TRACES OF CL. IF FINALLY MADE ANODIC, THEN THE O.C.V. IN NEW ELECTROLYTE IS 1.5 V. THIS EFFECT PROPORTIONAL TO C.D. & TIME OF ELECTROLYSIS. "A SUDDEN LARGE INCREASE OF IMMERSED SURFACE CAUSING A SUDDEN FALL IN POTENTIAL".
SMALE	PT. BLACK	———	1.35	O.C.V. AFTER EVOLUTION OF H_2 & O_2 BY IMPRESSED CURRENT.
BAIN 1943	FRESHLY HTD GREY Rh	$1N H_2SO_4$	1.30	FRESHLY HEATED Ir ALSO GAVE SIMILAR RESULTS; BOTH ELECTRODES GAVE POOR REPRODUCIBILITY & CONSTANCY.
BOCKRIS & HUQ 1956	BRIGHT-PT	$0.01N H_2SO_4$	1.24	AFTER PROLONGED ANODIC PRE-ELECTROLYSIS, "THE MEAN VALUE IS 0.01V HIGHER THAN $(e_0)O_2$" POSTULATES EQUILIBRIA BETWEEN PT-OXIDES; OR PTO_3 (UNSTABLE). POT. FELL AFTER 1 HR. POSTULATES TRACES OF SO_2 FROM H_2SO_4
BARNARTT 1959	AU	$0.1N H_2SO_4$	1.43 TO 1.36 AFTER ANODIC PRE-ELECTRO.	ATTRIBUTED TO "A REVERSIBLE AU/AU_2O_3 HYDRATED POTENTIAL." HOWEVER X-RAY DIFFRACTION GAVE NO DIFFRACTION LINES.
BRATZLER 1950	VARIOUS CARBONS	KOH	1.24 - 1.37	DEPENDING ON ASH CONTENT OF THE CARBONS, & WATER-REPELLANT PROPERTIES
POPAT 1960	PLATINIZED CARBONS	25% KOH	1.24	FOR 2 HOURS OR MORE; RECHECKED SEVERAL TIMES; INITIAL VALUE 1.3V WET PROOFED WITH TEFLON SUSPENSION.
POPAT 1960	PT BLACK	———	~1.84	$O_2 \mid \text{PT BLACK IN } H_2SO_4 \,\vdots\, \text{IN KOH M} \mid H_2$

This apparently anomalous effect has not been treated or mentioned in recent publications. The most important variable in this connection is the pH difference at the anode and the cathode as discussed previously.

b. At High Temperature With Molten Electrolytes:

Table 11 gives the experimental values of the O.C.V. of H_2/O_2 fuel cells at high temperatures together with the thermodynamic values at these temperatures. The peroxide mechanism at these high temperatures is not likely to be involved. Nernst equation apparently cannot explain these results satisfactorily.

Miscellaneous Observations

Some miscellaneous experimental results and observations obtained during this work are summarized in Appendix C.

SUMMARY OF OBSERVED OPEN CIRCUIT OXYGEN ELECTRODE POTENTIALS HIGHER THAN THE THERMODYNAMICALLY CALCULATED VALUES AT HIGH TEMPERATURES

TABLE 11

HIGH TEMPERATURE; FUSED ELECTROLYTE - Li-Na-K CARBONATES; H_2/AIR FUEL CELLS

FROM: FUEL CELLS; G. J. YOUNG, EDITOR; A C S SYMPOSIUM, 1960

AUTHORS	CATHODE MATERIAL	T °C	O.C.V. EXPT.	O.C.V. FROM ΔG° APPROX.
CHAMBERS & TANTRAM	SILVERIZED ZNO	600	1.3	1.032
		585	1.3	1.035
		640	1.27	1.03
BROERS & KETELAAR	AG	665	1.24	1.03
GORIN & RECHT	AG	700	1.21	1.025
	AG	750	1.25	1.02
	Li-NiO	700	1.23	1.025
DOUGLAS	AG	500	1.21	1.04
	AG	550	1.25	1.035
	AG	660	1.31	1.032
	AU	550	1.23	1.04
	AU	600	1.23	1.032

5.0 Discussion of Results:

It is shown in Appendix A that a plot of voltage vs log current density for the oxygen electrode or for H_2/O_2 fuel cells does not follow the so-called Tafel relationship. It is also clear from the polarization plots (with and without IR corrections) reported in this and the preceding reports that the entire polarization curve consists of two distinct sections (a) an initial small section involving a rapid drop in the emf at very low current densities (usually < 10 ma/cm^2) (b) a linear portion extending to fairly high current densities. In some of the latest experiments with liquid electrolytes, the linear portion extends to over 700 ma/cm^2. On the basis of the experimental facts reported here, it is assumed that these linear and non-linear portions of the polarization curves represent different mechanisms. Therefore, these two sections are treated separately. Since the linear section is of primary importance for the fuel cell performance, and since it is fairly well-characterized, it is treated first. Only the summary is given here. Details are given in Progress Report No. 17.

A Tentative Interpretation of Linear Polarization Plots:

Assumption: The only assumption made here is that the extrapolation of the linear portion to zero current density is valid. At present no theoretical justification for this empirical assumption is available, although considerable experimental justification is apparent from the fairly comprehensive experimental data presented. Such an extrapolation is not uncommon in other electrochemical systems, particularly in polarographic investigations where similar extrapolation of the linear section of the polarization plot to zero current density is well established and is characteristic of the redox couple under consideration. It will be shown below that such an extrapolation in the present case is very instructive.

6.0 Experimental Observations:

A careful examination of the linear polarization plots given here leads to the following important observations:

(1) Practically all the polarization loss or voltage drop occurs at or near the open circuit conditions, particularly with platinum black catalysts.

(2) The extrapolated value of the emf is approximately 0.93 ± 0.02 volts. That is, the extrapolated value of the polarization loss is nearly constant and approximately 0.3 volts.

(3) The extrapolated value of the emf is nearly independent of (a) pH (b) cell temperature up to about 200°C and gas pressures (c) Physical nature of the electrolyte, that is, whether the electrolyte is liquid, solid ion-exchange membrane type, held in an inert matrix or is in form of a paste, (d) different electrode structures and cell designs reported here.

(4) The extrapolated value of the emf of these cells is apparently little affected by the chemical nature of the catalyst material. This, however, may not be true for all catalysts under all experimental conditions.

(5) Different catalysts do change the slope of the linear sections. With platinum black electrodes, the slope after IR correction is negligible as shown by nearly constant IR-free emf over a wide range of current density. With other catalysts, such as Pd, Ni, Ag etc. the IR free polarization plots have a finite slope. With these catalysts, an increase in temperature apparently reduces the slope to a smaller or greater extent depending on the physico-chemical properties of the catalyst and the operational parameters.

On the basis of the above experimental observations, the following tentative conclusions can be made:

(1) The extrapolated value of the emf (i.e. approximately 0.93V) appears to be nearly independent of the usual rate parameters such as the catalyst material, pH of the bulk electrolyte, temperature of operation and other operational parameter.

(2) The polarization loss of approximately 0.3V appears to be a specific property of the fuel cells or electrochemical cells involving H_2 and O_2.

It would follow from the above that the nearly constant polarization of 0.3V may not be associated with the conventional activation polarization or slow (rate limiting) steps and that no catalyst is likely to be found which would raise the IR free, nearly horizontal line from 0.93V to approximately 1.23V. In other words, platinum black appears to be the best catalyst as judged by essentially zero slope of the line.

The above observations and tentative conclusions also suggest that an energetic or thermodynamic approach or analysis of the various processes involved might reveal the major cause of the irreversibility or polarization loss associated with the overall reaction (1) carried out electrochemically.

A summary of the energetic and thermodynamic aspects discussed in detail in Report No. 17 is given below.

7.0 Fundamental Thermodynamic Facts:

From the first law, the second law and the definition of the Gibbs free energy function (G=H-TS), it was shown that the maximum useful work, $-W_u$, obtainable from a chemical change carried out at constant temperature and pressure is given by:

$$-W_u = (\Delta G - T\Delta_i S) = \Delta H - (T\Delta S)_{rev.} - T\Delta_i S$$

where $\Delta_i S$ maybe defined as Clausius' uncompensated entropy change due to irreversibility and other terms have the usual significance (27). For an irreversible process, $\Delta_i S > 0$, hence $-W_u$ is always less than ΔG. Note that ΔG and ΔH being point functions are independent of the path, whereas W_u and $T\Delta_i S$ are dependent on the particular path or manner in which the change is carried out. Thus for instance, if H_2 is burned in an open container, all the free energy change, ΔG, is dissipated as $T\Delta_i S$ and the useful work is zero. The particular path under consideration here is the electrochemical path since in order to convert the available free energy of the overall reaction (1) into useful electrical energy, it is necessary to carry-out the reaction (1) electrochemically in a galvanic cell consisting of two separate electrodes connected internally by an electrolyte. All the energetic considerations discussed here are with reference to this electrochemical path only. The problem is to determine the magnitude of $T\Delta_i S$ and to ascertain its possible cause for the fuel cell systems involving H_2 and O_2.

8.0 Fundamental Electrochemical Facts:

1. Electrochemical process at the anode always involves oxidation, that is, transfer of electrons through the external circuit to the other electrode whereas the electrochemical process at the cathode always involves reduction, that is, combination with electrons.

Therefore, in effect, an anode produces an acid and a cathode produces a base (or utilizes an acid) whenever a finite faradaic current is drawn from the cell.

2. From the faradaic efficiency experiments reported by different investigators and discussed in the next section, it is shown that four faradays are obtained per mole of O_2 consumed. Further, literature evidence is presented showing that at catalytic electrodes, any peroxide, if at all formed, probably decomposes rapidly and electrochemically. These facts in essence mean that oxygen is substantially completely reduced to OH^- ions at the cathode.

   In view of all the available experimental results, it is postulated that from an energetic or energy conversion point of view, the effective or net anodic and cathodic reactions in weak as well as strongly acidic, strongly alkaline and neutral media, are probably as follows:

   Anodic reaction: $H_2 = 2H^+(aq) + 2e$

   Cathodic reaction: $\frac{1}{2}O_2 + 2e + H_2O = 2OH^-\ (aq)$

   The overall electrochemical reaction between H_2 and O_2 is therefore postulated as:

   $$H_2 + \tfrac{1}{2}O_2 = \underset{\text{(at the anode)}}{2H^+} + \underset{\text{(at the cathode)}}{2OH^-}$$

   It may be noted that energetically this overall electrochemical reaction is quite different from the gross reaction (1) which assumes or implies the formation of undissociated water molecule as the overall electrochemical process, without introducing any pH changes at each electrode. It is suggested that for a given system, any scheme of detailed reaction mechanism at each electrode must be energetically equivalent to the above net reactions, because any scheme will involve changes in the oxidation states of the reacting species thus creating a concentration or pH gradient at each electrode and since the amount of dissipated energy $T\Delta_1 S$ remains nearly constant regardless of the detailed mechanism.

3. Since the electrical neutrality of the system components must be maintained at all times, the anodic half-cell reaction cannot occur unless a simaltaneous cathodic half-cell reaction also occurs at the other electrode.

4. Regardless of the detailed mechanism of the ionic current transport through the electrolyte, it is well known that the cations migrate to the cathode and the anions migrate to the anode.

> In the case of H_2/O_2 fuel cells involving neutral, acidic or alkaline electrolytes (including ion-exchange membranes) and in the absence of any added inert electrolyte, H^+(aq) and/or OH^-(aq) will be involved in the transport of ionic current through the electrolyte. There is considerable energy involved in the creation of pH gradients associated with the electrode reactions and this must be dissipated during or following the electrochemical step, perhaps during the ionic transport processes.

The thesis or view advanced here is therefore that pH gradients are inevitable during a current flow in any electrochemical cell involving H_2 and O_2 thus making it practically impossible to maintain both the anode and the cathode at the same pH. Therefore the value of 1.23V is practically unattainable. This ionic concentration polarization in the immediate vicinity of each electrode is considered to be the primary cause of the irreversibility or polarization under consideration. The free energy associated with this pH gradient is believed to be dissipated as heat or $T\Delta_i S$ during the ionic transport which tends to equalize the pH of the bulk electrolyte. Under the conditions represented by the IR free, linear portion of the polarization plots, particularly with platinum black electrodes, the pH in the immediate vicinity of each electrode apparently assumes a saturation value resulting in a nearly constant polarization of 0.3 volts. Assuming that two faradays are transferred per mole of hydrogen gas reacted, this polarization is equivalent to approximately 14 Kcal of free energy dissipated into $T\Delta_i S$ or irreversible heat. Perhaps an alternate and more instructive approach may be to consider the energetics of the neutralization reaction:

$$H^+(aq) + OH^-(aq) = H_2O$$

The free energy change, ΔG, for this reaction is given by

$$\Delta G = \Delta G^o + RT\ln Q = -RT\ln K + RT\ln Q$$

where Q is a constant having the same form as the thermodynamic equilibrium constant K but in which the activities refer to the actual values of the reacting species under experimental conditions. For the anodic and the cathodic processes represented by the linear polarization plots, the values of the activity of H^+ at the anode and of OH^- at the cathode cannot be determined separately or independently and therefore ΔG is unknown. It may be recalled that only for an arbitrarily defined, hypothetical standard state, where all the products and reactants under equilibrium conditions are assumed to be at unit activity, $\Delta G^o = -RT\ln K$ since Q assumes a value of unity. This however is not the case under the conditions of a fuel cell operation. It is not yet established whether the numerical identity of the 14 Kcal calories as the "dissipated free energy" $T\Delta_i S$ with the so-called "heat of neutralization" of an acid by a base is an interesting but irrelevant coincidence or whether this identity has any fundamental significance.

It is speculated that the so-called "heat of neutralization" in reality might not be ΔH but $T\Delta_i S$ that is, irreversible heat of mixing representing the dissipated free energy ΔG (not ΔG^o) associated with the irreversible neutralization reaction. At present, however, there appears no unequivocal experimental method to prove or disprove this speculation. In any case, it is suggested that the mixing of an acid with a base or neutralization is a microscopically irreversible process and as such cannot in practice be carried out in a thermodynamically reversible manner. The electrochemical combination of H_2 and O_2, *in effect*, must involve such an irreversible step. This view, however, remains to be proved conclusively. An investigation of the pH and the temperature profiles as well as the location of the zone where the product water is actually formed in cells with varying pH of the bulk electrolyte, though very difficult, should yield very valuable information in this connection.

The thesis concerning the primary cause of irreversibility advanced here would predict that during the electrochemical decomposition of water to generate H_2 and O_2, the shape of the IR-free polarization (i.e. charging) curve should be similar to the IR-free discharge curve and that the IR-free voltage required for the generation of H_2 and O_2 under the conditions corresponding to the linear section of the polarization (i.e. after the pH saturation at the electrodes) must be approximately 1.23+0.3 or 1.53 volts. This is because $T\Delta_i S$ is always positive and must be added to the reversible voltage for the charging process. This 14 Kcal per mole of H_2 produced may be considered as the energy of demixing or dissociation of H_2O into H^+ at the anode and OH^- at the cathode which in effect must occur before or during the evolution of O_2 at the anode and H_2 at the cathode respectively. A literature review of the best known electrolytic cells offers some limited support to this prediction as shown in figure 15. This prediction, however, must be confirmed by more extensive experiments.

The relationship between the various forms of energy ~~under~~ the condition discussed above is summarized in Table 12.

It was suggested in the preceding progress report that it might be possible to calculate the value of $T\Delta_i S$ from the published values of single ionic entropies of migration transport for H^+ (aq) and OH^-(aq) at 25°C; and the value for $T\Delta_i S$ was shown to be approximately 14 Kcal. Further analysis of the problem however raises some uncertainty concerning the applicability of the literature data to the case under consideration and also concerning the assumptions made; namely, that $2H^+$(aq) and $2OH^-$(aq) are involved in the transport per mole of H_2 reacted. This aspect needs further examination.

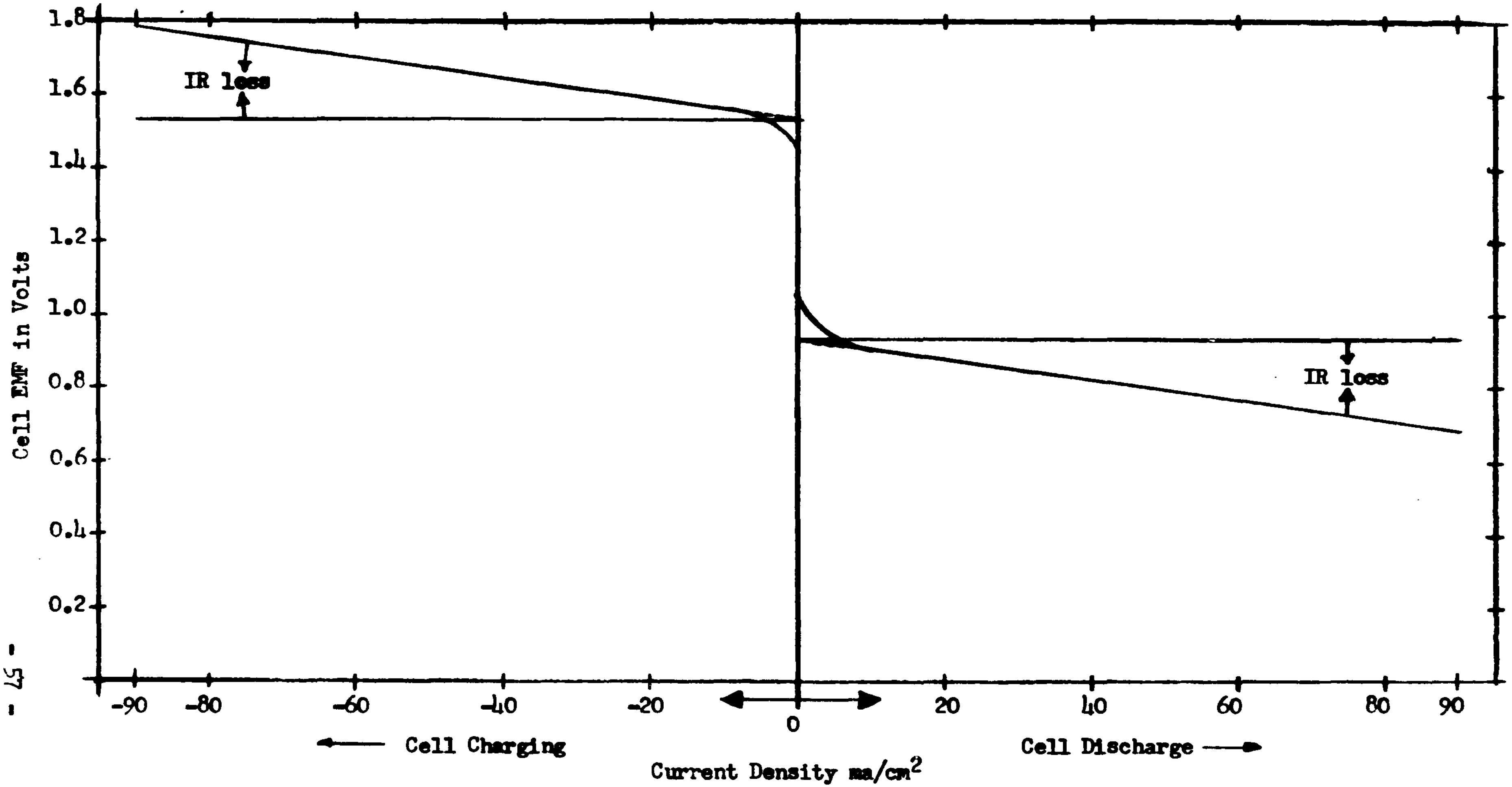


Figure 15

Current-Voltage Characteristics of a Regenerative H_2O_2 Fuel Cell
Niedrach and Gilman (67)

TABLE 12

Relationship between Useful Work (W_u), free energy, (ΔG) and Dissipated Energy ($T\Delta\, _iS$) in electrochemical cells involving hydrogen and oxygen in aqueous electrolytes, at 25°C and one Atmosphere

	Fuel Cell Discharge	**Generation of H_2 and O_2 from Water**
Reaction:	$H_2 + \frac{1}{2} O_2 \longrightarrow H_2O$ (1)	H_2O (1) $\longrightarrow H_2 + \frac{1}{2} O_2$
ΔG	-56.7 Kcal = -2.46 Volt Faradays	+ 56.7 Kcal = + 2.46 Volt Faradays
$T\Delta\, _iS$	+13.7 Kcal = +0.6 Volt Faradays	+ 13.7 Kcal = 0.6 Volt Faradays
Work	Output = + 43 Kcal = + 1.86 Volt Faradays	Work Input - 70.4 Kcal = -3.06 Volt Faradays
Volts	Available * = -1.86/2 = -0.93V	Volts Applies + 3.06/2 = $^+$ 1.53 Volts

*This assumes a change of two faradays (or two electrons) for each H_2 reacted or H_2O formed.

If the above interpretation of the irreversibility of electrochemical reactions involving H_2 and O_2 is correct, then it is possible to predict the magnitude of polarization losses associated with H_2 and Cl_2 or H_2 and Br_2 cells. The $T\Delta S$ quantity for the irreversible mixing of $H^+(aq)$ and $Cl^-(aq)$ or $H^+(aq)$ and $Br^-(aq)$ is probably negligible compared to that for H^+ and OH^-. Therefore the polarization loss associated with such cells could be made relatively small or negligible. Some published data show this to be the case.

Experimental verification of pH gradients

The following experiments and observations support the conclusion that it is practically impossible to carry out the electrochemical combination of H_2 and O_2 to form water or its reverse without creating a pH change at each electrode.

1. An H_2/O_2 cell was set up using platinized platinum electrodes and a neutral solution of sodium sulfate contained in an H shaped glass cell whose two compartments were separated by a fritted glass disc (See Figure 16). After a small current drain the anolyte and the catholyte were tested for pH change by (a) Phenolthanlein indicator (b) pH measurements. The anolyte showed distinctly acidic pH while the catholyte had turned alkaline. The measured pH change was approximately 5. Similar observations with acidic electrolyte have been reported by Mond and Langer (34) and by Patric and Wagner (28) among others.

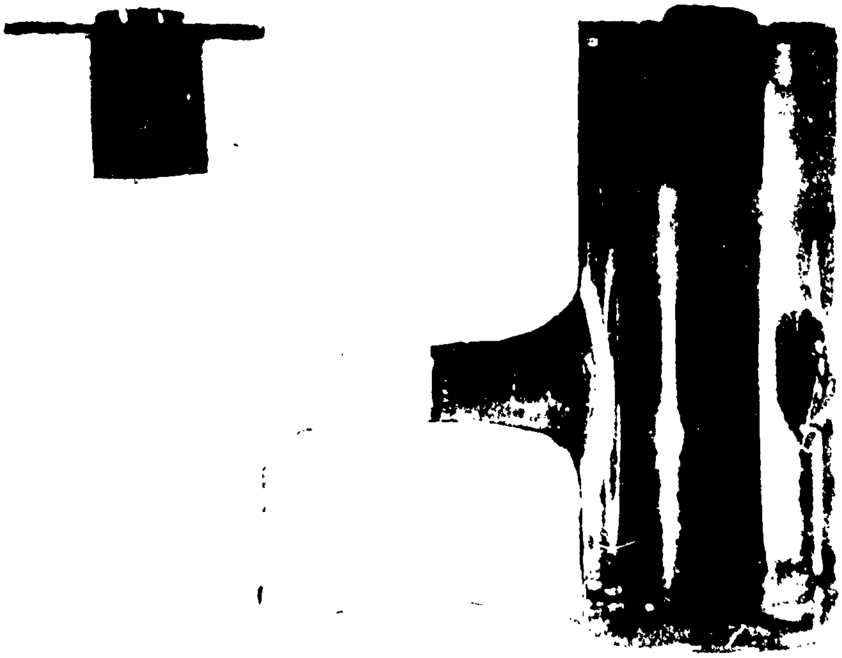
2. Hauel (20) reported the following pH changes in the anolyte and the catholyte for H_2/O_2 fuel cells with platinized carbon electrodes:

		Final pH		Total
Electrolyte	Initial pH	Anolyte	Catholyte	Amp. Hrs.
IM Acetic Acid IM Na-Acetate	4.6	4.6	10	0.16
0.4M K_2SO_4	6.0	2	13	0.375
IM $NaHCO_3$	7.8	8	10	0.041

3. The manufacture of an acid and a base by electrolysis of the neutral salt solution at inert electrodes is a well known process (29). This would not be possible if the electrolysis were not accompanied by pH gradients at each electrode.

How to attain "quasi-reversible emf" of H_2/O_2 cells or O_2 electrode?

From the above discussion it is clear that starting with a homogeneous electrolyte of a given pH, it is not likely to obtain a reversible emf for H_2/O_2 cells or O_2 electrode. However, if each electrode is well buffered at a suitable pH it should be possible to obtain an emf equal to or greater than the value of 1.23 volts.



These predictions were verified by using the H type cell shown in figure 16. The electrolyte contacting the oxygen electrode was 1.0 N H_2SO_4 and the electrolyte contacting the H_2 electrode was 1.0 N NaOH. The physical mixing of the acid and the base was virtually prevented or delayed by the fine fritted glass disc. The open circuit voltage exhibited by such a cell was over 1.84 volts. The open circuit voltage of the acid/base cell without H_2 and O_2 gases was slightly over 0.62 volts. However when the gases were reversed, the open circuit voltage was only about 0.4 volts as would be expected. These are only preliminary results though their essential validity was verified several times. If the exact pH at each electrode can be computed by an independent method, it may be possible to verify whether each half cell reaction at its buffered pH proceeds reversibly or not. Some approximate calculations suggest that each half cell reaction at its pH probably proceeds in a nearly reversible manner.

What is the nature of an acid/base concentration cell? Can it be used as a source of steady emf or electrical energy?

Since the acid/base concentration gradient is postulated to be the primary cause of irreversibility, it is pertinent to ask the above questions and to determine whether the discharge of an acid-base concentration cell (without any reacting gases) involves faradaic current (i.e. redox reaction at each electrode) or non-faradaic current. Bertholet (30) investigated such cells and he advanced the hypothesis that these cells do not involve any oxidation or reduction, that the chemical changes produce no change of valence and no liberation or formation of ions according to Faraday's laws, and therefore no electrochemical action. "If the only chemical change which occurs in the cell is not electrochemical, the energy of that chemical change cannot be a source of electromotive force." This important statement was made by Reed in 1904 (31). It would be most interesting and informative if the validity or otherwise of this statement can be established beyond doubt. In order to obtain any significant potential for any length of time from the acid/base cell, the two compartments (anolyte and catholyte) must be separated by a very high impedance agar bridge or frit since otherwise free mixing will occur. Even then the potential, after reaching a maximum, continuously drops with time. For the same reason, only extremely small transient currents could be drawn from such a cell and the cell potential dropped to a negligible value. These preliminary observations would suggest that acid/base cell discharge characteristics, in some respects, resemble a capacitor - discharge behavior. The fact that the potential of such a cell and its stability is markedly dependent on the area and the activity of the electrode material would appear to support such a view. Incidently, the polarity of the acid side in such a cell is positive and that of the base side is negative whereas in H_2/O_2 fuel cells, H_2 electrode is negative and O_2 electrode is positive. The pH gradient accompanying the H_2/O_2 fuel cell reaction must therefore set up the back emf as required by the law of mass action.

Some possible causes and interpretation of the different slopes of linear Polarization plots with different catalysts.

It has been definitely established that platinum black is the best known catalyst for the oxygen electrode. The platinum black supplied by the Englehard Industries Inc. appears to be the most active black as compared to the same weight of Bishop's Platinum black or electrochemically deposited platinum black. Different methods of reducing the chloroplatinic acid to platinum black also give catalyst with different slopes. The most obvious cause for this would appear to be the particle size and differences in the real area for a given weight or for a given geometric area. Since the current density used is based on apparent or geometric area, it does not provide a satisfactory basis for comparison.

Another possible cause for the different slopes is the differences in the chemisorption properties of O_2 on different materials. Thus for instance, porous carbon, in spite of a large specific area must have relatively poor chemisorption properties for O_2 since, by itself, uncatalysed carbon is the poorest electrode material for oxygen electrode. This aspect of chemisorption is inherently related to the catalytic activity of the various materials. Detailed mechanism of the functioning of the catalyst in presence of various electrolytes is not yet established and therefore will not be discussed any further. For porous gas diffusion type of electrodes, pore structure and size is also important since with such electrodes performance on air is poorer than the performance on pure oxygen. Oxygen from air is apparently unable to reach all the available active sites and the effective three-phase reaction zone is correspondingly reduced.

Because of the complexity and interdependence of all the above parameters, a simple or definite interpretation is not possible at this time. Probably each catalyst system for a given electrolyte will have to be treated separately for an interpretation of IR-free linear plots having slopes substantially greater than zero.

Discussion of Results on Open-circuit and in the Non-linear Region.

9.0 A Brief Review of the Theories of the Oxygen Electrode Irreversibility

Since a critical review of the various theories on the subject has already been presented in the Progress Report No. 17, only a brief summary of these, with emphasis on some of their limitations will be given here. These theories may be classified as (1) the oxide theory (2) the peroxide theory (3) the mixed potential theory involving impurity effects (4) the theories involving irreversible heats of chemisorption.

1. The oxide theory: Around 1910, this theory was widely accepted as the most probable major factor responsible for the irreversibility of the oxygen electrode. The theory assumes that the so-called oxygen electrode potential is determined primarily by the couples involving the metal and its oxides (32). The metal most widely used was platinum. No direct proof of the theory was, however, available and it was necessary to postulate the existence of several unstable or unknown oxides and hydrates of Platinum in the higher oxidation states in order to interpret the potentials higher than about 0.93 volts (32). In 1933, Hoar (33) modified the above view and suggested that the low open-circuit voltage of the oxygen electrode is not so much due to the oxides but due to the permeability of the surface oxide film to the electrolyte. This, in Hoar's view, gives rise to "self-polarization." Accordingly, a perfectly impermeable oxide film should give the reversible oxygen electrode potential, whereas a very porous film should give the lower metal-metaloxide potential. This conclusion, however, is contrary to the experimental fact that the platinum black (chemically or electrochemically reduced from platinum salts) gives the highest, most reproducible and most stable potential for the oxygen electrode as compared to the bright, oxidized or gray platinum. Hoar's view was also criticized by Bain (22) and later by Bockris and Hug (23) primarily because of its implication that the theoretical oxygen electrode potential could never be attained under actual experimental conditions. This is contrary to the experimental observations of several investigators as reported in Table 10. Some of the other serious objections and limitations to the oxide theory in general are summarized below. **(See note at top of Page 66).**

(a) In alkaline systems, different electrodes such as platinum black, palladium black, nickel, silver and other materials like activated carbon (which does not form a stoichiometric, discrete, three dimensional oxide) give approximately the same (viz 1.12 volt) open circuit voltage. It is highly unlikely that different metals and carbons would give stable oxides with the same potential.

(b) It is experimentally observed that the oxygen electrode potential is dependent both on the electrolyte pH as well as on the partial pressure of oxygen (though not in conformity with the thermodynamic predictions). It is difficult to explain this dependence on the basis of the oxide theory without attributing a certain amount of electromotive activity to the oxygen itself.

(c) The so-called theoretical or thermodynamic values of the "standard potentials" of the metal-metal oxide couples of noble metals do not appear to be experimentally measured values but are only approximate values calculated on the basis of several as yet unverified assumptions. Thus, for instance, the exact nature and stoichiometry of the various chemical and/or electrochemical reactions or intermediates are not established and secondly their actual activities are unknown. Apparently it would be extremely difficult to calculate with any degree of accuracy the thermodynamic values of the potential associated with the different oxides. Also, if the equilibria such as $Pt^{++} + 2e \rightleftharpoons Pt$ are involved it would be apparently incorrect to apply the Nernst equation since the concentration of Pt^{++} ions in absence of any externally added platinum salts would be negligibly small and far below the limits of analytical detection. Secondly, the Nernst equation applied to the $Pt^{++} \rightleftharpoons Pt$ couple would give lower (less noble or more anodic) potentials as the activity of Pt^{++} goes down to negligible values whereas the experimental values are higher than the reported standard oxidation potential for platinum of approximately 0.93V. Thirdly, any assumption involving oxidation states of platinum higher than Pt^{++} would be difficult to establish for conditions under consideration here since the stability should rapidly decrease with higher oxidation states (valence) of platinum as pointed out by Richards (19).

(d) Several attempts to identify the nature and stoichiometry of the superficial metal-oxygen complex (often loosely and perhaps incorrectly described as oxides) have been reported in the literature, particularly in connection with the electrochemical passivity of metals. Two principal views exist on this subject. One view supported by Uhlig (35), Kolotyrkin (36), Giner (37), Hackerman and Popat (38), among others, attributes the electrochemical passivity to a chemisorbed layer of oxygen to the extent of approximately a monolayer or less. The other view, supported by Evans (39), Bonhoeffer (40), Vetter (41) and other German investigators is that the electrochemical passivity accompanying the anodic evolution of oxygen (instead of metal dissolution) is caused by a discrete, three-dimensional, stoichiometric oxide film on the passive metal (including platinum). For the anodic evolution reaction on platinum, Kolotyrkin (36) maintains that in the case of platinum the absence of oxide layers on the surface of the metal in the investigated region of polarization "is a firmly established fact."

On the other hand, Lingane (42) among others, claims that the formation of discrete oxide film on platinum and gold during anodic polarization "is now an established fact." Laitinen and Enke (43) reported approximately one atomic layer of oxygen during the oxygen evolution on platinum and suggested that although the formation of the oxide is energetically favorable at potentials lower than that required for oxygen evolution, the oxide formation reaction is immeasurably slow.

(e) Concerning the metal-oxygen interaction, examination of the oxygen adsorbed from gas phase on platinum carried out by Chapman and Reynolds (44) shows an amount less than that sufficient to give a complete monolayer of Pt O. Armstrong, Himsworth and Butler (45) claim that there exists no evidence for the presence of a platinum oxide film on platinum. Moeller (46) states that platinum shows no reaction with oxygen at ordinary temperatures. Barnartt (24) attempted to obtain the x-ray diffraction patterns of the anodically formed (visible) films on gold but did not observe any diffraction lines. Similar attempts for platinum by other investigators have all been apparently unsuccessful.

(f) Results by Cohen et al (47) on the calorimetric titration of adsorbed oxygen on platinum black by free hydrogen for obtaining a "clean" reproducible surface show absence of any bulk oxide.

(g) During the fuel cell discharge in a H_2/O_2 fuel cell, the net reaction at the oxygen electrode is cathodic reduction of oxygen, that is, addition of electrons from the external circuit. Under these conditions it is difficult to see how the metal atoms can lose their electrons and be oxidized.

(h) No difference in the open circuit voltage of the oxygen electrode is observed before and after the platinum black is treated with hydrogen gas or after treating it cathodically in an electrolytic cell.

(i) Oxide formation would appear to be a slow process whereas the response of the oxygen electrode to the variations in the load resistance over a wide range of current density is relatively fast.

On the basis of the various lines of reasoning and experimental evidences, it would seem that bulk oxide formation is not likely to be responsible for the polarization loss of the oxygen electrode on open circuit and in its cathodic reduction during the fuel cell discharge.

NOTE:

In a more recent publication (1956) Hoar (48) has apparently modified or changed his views concerning the mechanism of the anodic evolution of oxygen and has suggested that the rate-limiting step does not involve electron-transfer reaction. In his view any electrode surface in alkaline solution is covered with a strongly adsorbed layer of OH^- and that the rate-limiting step is likely to be $OH + OH^- \rightleftharpoons (OH \leftarrow OH)^-$ which suggests some kind of interaction (as yet not clearly defined) between OH^- ions and OH radicals. The view that probably OH^- ions are strongly adsorbed on the oxygen electrode is similar to the conclusion arrived at in the present studies.

The peroxide theory: According to this theory, the potential of the oxygen electrode on open circuit and under finite current flow is determined by the reduction of oxygen to peroxide which involves only two faradays per mole of O_2 (see equations 5 and 6) instead of its complete reduction which involves four faradays per mole of O_2 (see equations 3 and 4). The theory assumes that the peroxide species so produced is stable or else is decomposed chemically and not electrochemically and that the Nernst equation involving four electrons per mole of O_2 is therefore not applicable.

The assumption that H_2O_2 or HO_2^- may be an intermediate product in the cathodic reduction of oxygen on many electrodes is not new. In 1882 Traube (49) showed that the presence of oxygen at several cathodes caused the peroxide formation under certain conditions. This and subsequent studies emphasized the fact that the current efficiency for the peroxide formation was governed primarily by the physical nature and chemical properties of the electrode material, that is, on the catalytic properties of the electrode material.

From this catalytic point of view, the electrode materials can be arbitrarily divided into two groups: (1) Those materials on which the peroxide is not decomposed at a significant rate and which can therefore be used, at least in principle, for the cathodic manufacture of H_2O_2. Mercury, graphite and certain uncatalyzed carbons belong to this group. Mercury, because of its high polarization for H_2 and O_2 electrodes and because of certain toxic or undesirable physical and chemical properties is practically never used as a material for the oxygen electrode and will not be considered here. (2) Those materials which decompose the peroxide species more or less completely depending on the surface nature and the catalytic property of the material. Platinum, palladium, silver and other noble metals and alloys as well as transition metals like nickel, iron, and cobalt may be included in this group. For highly acidic electrolytes such as 6N H_2SO_4, the choice of electrode material is limited to noble metals (or special alloys) due to corrosion problems.

Even more important than the chemical nature of the electrode material (provided it is corrosion resistant) is the surface activity and the surface area. Thus, for instance, platinum black is one of the best known catalysts for the hydrogen peroxide decomposition and is also the best known electrode material for the oxygen electrode. Bright [illegible] smooth platinum on the other hand is relatively poor material for the peroxide decomposition and is also a poor material for the oxygen electrode.

Current density, electrolyte pH and temperature are other important factors to be considered. Also it must be noted that hydrogen peroxide has the duel ability of being reduced at a cathode and of being oxidized at the anode. Thus for instance in a typical study (50) hydrogen peroxide produced at the cathode migrated to the zinc anode and depolarized it, causing corrosion of approximately 40% to 70% more than the amount of zinc dissolved by the current. The overall cell voltage must also be affected thereby.

The most important tests for the peroxide mechanism would include determination of (a) whether it obeys the Nernst equation under the given experimental conditions when the open circuit (rest potential) is approached from either anodic or cathodic direction (b) whether the experimental value of the standard potential thus obtained agrees with the thermodynamic value and (c) whether the peroxide is decomposed chemically or electrochemically.

Carbons: In 1943 W. G. Berl (51) published an important paper concerning the behavior of the oxygen electrode on graphite (in absence of any catalysts) in alkaline solutions to which known quantities of hydrogen peroxide were added. He showed that uncatalyzed graphite electrodes in alkaline electrolytes and in the presence of peroxide species, approximately obey the Nernst equation for the peroxide mechanism involving two faradays per mole of O_2 as given by reaction (6) and equation (E). Berl did not study the effect of weakly alkaline, neutral or acidic pH or the effect of partial pressure of oxygen. Also he did not apparently investigate the open-circuit behavior of the oxygen electrode with or without the peroxide addition. For the standard potential for the oxygen-peroxide couple he obtained, on the basis of his experimental data, a value of 41.6 mv as compared to the thermodynamic value of 74.5 mv reported by Latimer (1). Within these limitations and observations, Berl interpreted his results in terms of the peroxide mechanism. Since then, however, there is apparently an increasing tendency in the literature to attribute the irreversibility of the oxygen electrode at almost all materials (catalytically active) in all electrolytes and in absence of added peroxide to the peroxide mechanism. Thus, for instance in 1954 Yeager and co-workers (52) made a statement (subsequently modified) that "many vain attempts to obtain the theoretical value for the H_2/O_2 cell in aquous media were based on the ignorance of the fact that oxygen is first reduced to peroxide."

Their latest view (53) however, describes the scope and the conditions for the applicability of the Nernst equation for peroxide control (equation E) more accurately: "this equation has been shown to be followed for non-polarized graphite as well as porous carbon electrodes containing no peroxide decomposing catalysts for HO_2^- concentrations from 10^{-4} to 1 M, OH^- concentrations from 10^{-4} to 10 M and O_2 pressures from 0.2 to 35 atm." It is implied in this statement that the validity or applicability of the peroxide mechanism is not established for electrodes which possesshigh catalytic activity for the decomposition of the peroxide or for neutral and acidic electrolytes in the absence of added peroxide.

Oxygen electrode for fuel cells almost always has the property of decomposing any peroxide, if involved more or less completely and rapidly. Hence, the above mechanism may no longer be applicable. The fundamental problem concerning the validity of the Nernst equation when the effective concentration of one of the reacting species is negligibly small ($< 10^{-6}$M) has already been discussed. Furthermore, the value of the activity coefficients and the effective concentrations of the relevant ionic species at the electrodes are generally not known. In spite of these difficulties Kordesch (54), for instance has apparently interpreted his results on the basis of the peroxide mechanism. He states, "When special peroxide decomposing catalysts are used, the hydrogen peroxide concentration is reduced beyond the sensitivity of analytical tests to an estimated value of 10^{-10} molar .... The low concentration of peroxide corresponds to the open circuit potential of 1.10 to 1.13 volts against the hydrogen electrode in the same electrolyte. This fact changes the two electron process to an apparent four electron mechanism." However, several investigators have conclusively shown as discussed later, that (1) the peroxide decomposition in electrochemical cells is an electrochemical process (not a chemical one) and that (2) the current efficiency for the oxygen utilization in fuel cells corresponds to four faradays per mole of O_2 consumed, that is 100% faradaic efficiency for the complete reduction of O_2 to OH^-.

Metallic Electrodes: Repeated attempts by several investigators to show the reversibility of the oxygen/peroxide couple at metallic electrodes have all been unsuccessful because of the catalytic decomposition of the peroxide at the electrode surface. Weisz and Jaffe (55) attempted to verify the Berl mechanism using porous, sintered silver and nickel electrodes. With the silver electrode in 5 molal NaOH they obtained a value of 0.043 volts (instead of 0.0295 volts) for the change in voltage corresponding to a 10 fold change in the peroxide ion concentration. With the nickel electrode, the change in voltage was zero for a 10 fold change in the peroxide concentration.

Winkelman (56) showed that cathodic reduction of oxygen on platinum was electrochemical in nature and depended on the electron-exchange properties of the platinum electrode. Vielstich (57) also investigated the cathodic reduction of oxygen at platinum, nickel, carbon, silver and silver oxide electrodes and suggested that the overall process involved a four faraday transfer per mole of O_2 reacted. Gerischer and Gerischer (58) showed that the decomposition of peroxide at platinum anodes in acidic as well as alkaline solution was electrochemical in nature and was initiated by electron transfer between metal and H_2O_2. Similarly, Hickling-Wilson (59) studied the anodic decomposition of peroxide at various electrode materials and showed that the process is electrochemical. The current efficiency in alkaline, neutral and acid media at all anode materials (Pt, Au, Ni, graphite and platinized Pt) was 100% provided the current density was not too high.

It therefore appears definitely established that the decomposition of hydrogen peroxide, if produced as an intermediate, is electrochemical in nature. Barak, Gillibrand and Gray (60) determined the current efficiency of oxygen utilization with moulded carbon electrodes containing silver catalysts in KOH at 25° and 60°C and obtained four faradays per mole of oxygen consumed at all current densities studied at the two temperatures. Similarly in Sulfuric Acid solutions with carbon electrodes containing palladium catalyst on platinum screen, four faradays per mole of O_2 were reported. Justi and Winsel (61) determined the current efficiency for their DSK electrodes in alkaline electrolyte at 21.5, 42.9 and 60.5°C and in all cases reported four electron efficiency per mole of O_2 used. These results indicate that the peroxide mechanism probably plays only a minor, if any role in the irreversibility of the oxygen electrode in fuel cell systems.

Other limitations of the peroxide theory are that it cannot explain the effect of various non-thermodynamic parameters on open circuit voltage of the oxygen electrode and the steady state polarization behavior of the H_2/O_2 cell in acidic and alkaline media on various electrode materials (except perhaps carbon in alkaline media) discussed in this communication. It is not implied that peroxide may not be an intermediate in the steady state operation of an oxygen electrode under finite current flow conditions. It is suggested, however, that the peroxide theory does not satisfactorily explain the polarization behavior of the oxygen electrode on open circuit or at significant current densities.

The mixed potential theory:

This theory postulates that the unattainability of the reversible oxygen electrode in "normally purified" solutions is due to the presence of trace impurities in such solutions.

The velocity of simultaneous electrode reaction involving these impurities at the electrode is assumed to be much greater than the exchange current for the oxygen evolution reaction. This view was proposed by Bockris and Huq (23) in an attempt to explain the effect of the so-called pre-electrolytic purification of the electrolyte before the oxygen evolution reaction on bright platinum in sulfuric acid solution under externally applied voltage. Since the amount of trace impurities postulated is of the order of 10^{-11} moles per liter or less and since the sulfuric acid itself is regarded as the source of this trace impurity (in absence of any other possibility), it would be practically impossible to either prove or disprove the presence of such trace impurities and their effect on the electrode potential. For the same reason and because of the vague and uncertain nature of the impurity effect, this theory apparently offers little hope of either predicting or reducing the polarization of the oxygen electrode on open circuit and during current flow. Other observations concerning the experimental results reported by Bockris and Huq include the following:

(a) The data reported are not steady state data since overvoltage measurements were made immediately after each successive decrease or increase of current density. Significant hysteresis is observed between the "first up" and the "first down" Tafel plots.

(b) If the solution was purified only cathodically at 10^{-2} amp/cm^2 for 36 hours, only 0.84V was obtained for the open- circuit voltage. Only after the solution was purified anodically at 10^{-2} amp/cm^2 for at least 48 hours, the potential obtained was $1.24^{+}-0.03$ volts. This potential was not steady however, and it fell after about one hour . If anodic pre-electrolysis was recommenced the potential of 1.24 volt was re-established for approximately an hour. The time of pre-electrolysis was only arbitrarily selected. The order of pre-electrolysis (cathodic followed by anodic pre-electrolysis) was apparently selected because the reverse order would not give such high values for the open-circuit voltage. Only H_2SO_4 solution was used as an electrolyte. Other electrolytes and particularly alkaline solutions would have been more decisive.

(c) Other investigators (see Tables 7 and 10) have obtained reproducible results without the pre-electrolytic purification. When anodic pre-electrolysis was used, time-dependent open circuit voltages greater than 1.23 volts were observed by several investigators as reported in Table 10. Bockris and Huq also stated that the mean value of the rest potential was about 10 mv higher than the thermodynamic value of 1.229v. The authors have attempted to explain these higher values on the basis of equilibria involving platinum oxides for which no reliable data are available as discussed earlier.

(d) The authors claim that the attainment of 1.24 volt is independent of the mode of electrode preparation. This is contrary to the experimental observations by several other investigators. Particularly the difference in the behavior of platinum black and bright platinum is marked as is well known.

The authors have apparently ignored the pH effect at or near each electrode during the prolonged pre-electrolysis. The anodic pre-electrolysis will produce acidic environment at or near the electrode and this will increase the rest potential as measured against a reference electrode. Cathodic pre-electrolysis, on the other hand will have the opposite effect. It is likely that the time dependence and anomalously high open circuit voltage could be caused by such pH changes since diffusion and equalization of concentration of ionic species under their experimental conditions would be a relatively slow process.

Theories involving heats of chemisorption: These attribute the open-circuit irreversibility of the oxygen electrode to heats of chemisorption. It is assumed that the chemisorption of the reactant gases is not a reversible process and that the heat of chemisorption is dissipated before the electrochemical step (62).

The predictions based on this theory are contrary to experimental facts. The theory would predict that "the greater the magnitude of the heat of chemisorption, the further the cell potential would be from that expected theoretically" (62). Thus for instance the reversible potential for the hydrogen electrode on open circuit should never be achieved since heat of chemisorption on platinum black is considerable. This is quite contrary to experimental fact since the reversibility of the hydrogen electrode at platinum black and palladium under certain conditions is well established. The reversibility of chlorine and bromine electrodes is also established, at least on open circuit. DeBoer (63) points out that no conclusive experimental evidence exists to show that chemisorption of gases is necessarily an exothermic or an irreversible process.

Adams (64) points out that as a rule the surface which exhibits high heats of adsorption would be more active catalytically than one with a low heat of adsorption. Accordingly, platinum black is a better catalyst for hydrogen and oxygen electrodes than bright platinum.

Also the Chemisorption theory fails to explain why the irreversibility or the rate of change of polarization should be much greater at extremely low current densities rather than at high current densities as observed experimentally. The theory also cannot explain why in strongly alkaline electrolytes, different electrodes (e.g. Pt, Pd, Ni, Ag. C) exhibit approximately the same open circuit voltage.

Undoubtedly the heat of chemisorption is an important parameter related to the activity of the catalyst under finite current flow conditions. However, it fails to explain the irreversibility on open circuit. Also it fails to explain the various experimental observations reported here.

Present status of the contemporary theories:

Experimentally it would appear to be extremely difficult to establish unequivocally the contribution of each of the above factors to the total polarization of the oxygen electrode in a given system or to show that they are not involved. This is because at present it is not possible to isolate and/or measure the vanishingly small traces of the postulated peroxides or impurities or to differentiate between the chemisorbed oxygen species and the so-called surface oxides. Also it would be extremely difficult to differentiate between the entalpy (ΔH) of chemisorption and the free energy (ΔG) of chemisorption using an independent method (i.e. not involving potential measurements).

On the basis of the preceding arguments and the experimental results presented here, it is believed that the above theories are likely to play only a minor role in the irreversibility of the oxygen electrode, particularly on open circuit and that the major cause (s) of this irreversibility must be sought elsewhere.

Role of Electrochemical Double Layer

It is suggested that in order to obtain a better understanding of the factors responsible for the irreversibility of the oxygen electrode, it will be necessary to investigate the nature and the structure of the electrochemical double layer (edl) and the mechanism of establishment of a potential difference at an interface. It is believed that a thorough understanding of the edl may provide a basis to correlate and interpret most of the experimental facts and may help in resolving or unifying the apparently conflicting views on the irreversibility of the oxygen electrode.

It is well known that when two or more phases (e.g. solid-gas-liquid) are brought into contact, there is established between them an electrochemical double layer due to an unsymmetrical distribution of ions, electrons or multipoles at the interface. Intimately associated with the formation of the edl is the establishment of a potential difference across the interface. The charge distribution and the associated potential difference at the interface can be brought about by (a) charge transfer across the interface (b) adsorption of ions (c) adsorption and/or orientation of dipoles (d) deformation of polarizable atoms or molecules at an interface due to an unsymmetrical force field.

All or most of these effects may operate simaltaneously at the oxygen electrode, thus complicating the structure of the edl and the distribution of the potential associated with it. The qualitative aspects of the edl at a mercury-electrolyte interface, approximating the ideal polarizable electrode and at the catalytically active metal/gas/electrolyte interface used in fuel cells have been reviewed in the progress report No. 17. A distinction was made between an ideally polarizable electrode and an ideally non-polarizable electrode. Thus the ideal polarizable electrode is characterized by the existence of an electrostatic equilibrium at the interface whereas an ideal non-polarizable electrode is characterized by an unhindered charge transfer across the interface. The potential exhibited by the ideal non-polarizable electrode is believed to be characteristic of the electrochemical reaction under consideration. Under the open circuit conditions for any real electrode, however, it would be difficult to measure or differentiate between the electrostatic and the electrochemical effects. Other problems encountered in the investigation of the edl at solid metal electrodes were discussed in the progress report No. 17 and are summarized below.

(a) The problem of defining and reproducibly obtaining a "clean" solid metal electrode.

(b) The problem of defining a "smooth" or homogeneous surface for a solid electrode and the uncertainty involved in extrapolating the results from the "smooth" electrode to the rough or porous electrodes and in comparing the results of various investigators using different methods of surface treatments.

(c) The problem of measuring "true" or "real" area for a given geometric area available for electrochemical reaction and the lack of agreement in the values of the surface areas or roughness factors obtained by different methods. Also there is some uncertainty whether the active area or sites remain constant or not as a function of time and/or current density. It maybe noted that the surface area is involved in all computations of current density and depending on the porosity, thickness and geometry of the electrode, the real area can be varied considerably for a given geometric area.

(d) The difficulties involved in measuring the edl "capacitance" and its variation with the method of measurement, the frequency of the a.c. signal used and the potential of the electrode as contrasted from the capacitance of the ordinary electrical capacitors.

(e) The difficulty in interpreting the edl capacitance data and the problem of differentiating between non-faradaic i.e. pure capacitance current and the faradaic current due to electrochemical reaction, particularly at very low currents near the open circuit potential.

(f) Some uncertainty involved in the value of the measured potential of a polarized electrode with respect to an arbitrary reference or probe electrode involving a luggin capillary at a finite distance from the test electrode.

Because of the above difficulties our understanding of the electrochemical double layer at solid electrodes and of the mechanism of establishment of a potential difference at such electrode has been quite limited. However, a satisfactory solution of these problems or difficulties appear essential in order to obtain a better understanding of the irreversibility associated with the oxygen electrode.

A Suggested, Tentative Interpretation of the Behavior of the Oxygen Electrode at or near the open circuit.

There is hardly any doubt that in order to explain the behavior of the oxygen electrode of H_2/O_2 cells on open circuit and at very low current densities, we must take into account not only the thermodynamic aspects of the overall reaction, but also the contribution of the electrical double layer and the associated phenomena under these conditions. However, one modification or simplification of the classical approach to the double layer concept is made for the purpose of the present discussion. Instead of considering the double layer capacitance and the associated potential at a single electrode (without considering the other electrode, as is done usually), the overall capacitance across both the electrodes, that is, the whole cell, will be considered here.

Assumptions:

(1) Linear and non-linear sections of the polarization plots indicate different mechanisms.

(2) A hydrogen-oxygen fuel cell on open circuit and in the non-linear portion of the polarization plots may be treated as an electrochemical generator plus an electrolytic capacitor.

These two assumptions are based on the experimental observations reported earlier in connection with the behavior of the H_2/O_2 cells at or near the open circuit and in the linear region of the polarization plots respectively. It is significant to note the similarity of the polarization plots for the H_2/O_2 cells or oxygen electrode with the classical polarograms. It will be recalled that the initial non-linear section of a polarogram is usually attributed to the capacitor current due to the charging of the double layer and the half-ware potential is obtained by the extrapolation of the linear section of the polarogram to the zero current. Thus in a polarogram also, the linear and non-linear sections of the polarogram represent different mechanisms.

Associated with the electrochemical potential and the electrostatic potential respectively will be two types of currents, viz faradaic current associated with the electrochemical part and electrostatic or capacitor current associated with the electrostatic part. It should be emphasized that these two types of voltages are inter-related and interdependent and that it is not possible to separate their effects. However, an arbitrary separation of the two effects is required in understanding or interpreting the behavior of the cell on open circuit and at low current densities. It is apparent that the charged capacitor represented by the cell acts, in effect, as a storage device for potential energy. Therefore, the electrostatic voltage, V_{dl}, associated with it must be distinguished from the electrochemical voltage, V_g or emf of the electrochemical generator. Thus, the open circuit voltage, V_{oc}, can be represented as:

$$V_{oc} = V_g + V_{dl}$$

It is convenient to further divide, again arbitrarily, V_{dl} into two parts: One part, designated as ΔV_{irr}, represents the irreversibility of the pH gradient due to faradaic current flow and a second part, designated as ΔV_c, representing all other effects, namely those due to relative surface areas of the electrodes, the surface energy, the dipole orientation, the polarizability or specific adsorption of various ionic and other species present, any contact potential differences, and all unknown effects not accounted for by ΔV_{irr}.

Therefore, $V_{oc} = V_g + V_{dl}$

or $V_{oc} = V_g + (\Delta V_{irr} \pm \Delta V_c)$

It may again be seen from the last equation, that V_g, ΔV_{irr} and ΔV_c are interdependent and that there seems no way to separate these effects. If V_{irr} is assigned a value of 0.30V at the saturation value of electrode pH as previously discussed then V_g assumes a value of 0.93V and therefore,

$$V_{oc} = 0.93\ V + (0.3 \pm \Delta V_c)$$

$$V_{oc} = 1.23 \pm \Delta V_c$$

On open circuit, the most important variable affecting the voltage of a cell of constant design and constant electrolyte and for a given method of measurement is ΔV_c. For fuel cell discharge, ΔV_c will normally have a sign opposite to that of V_g and therefore V_{oc} will usually be less than 1.23V.

The various effects can now be interpreted and explained in terms of changes in ΔV_c. As is well known, a charged parallel plate capacitor with a capacity, C, and a charge, q, will exhibit an electrostatic voltage across its plates in accordance with the equation:

$$\Delta V_c = q/C$$

The capacity of a parallel plate capacitor is governed by the equation:

$$C = \frac{DA}{4 \pi d}$$

Where D is the dielectric constant, A the area of each plate, and d the distance between the two plates. Therefore, for a constant charge, q, the change in the electrostatic voltage of the capacitor is given by:

$$\Delta V_c = \frac{4 \pi qd}{DA}$$

It may be noted that the dielectric properties associated with the double layer at each electrode are not the same as those of the bulk electrolyte. The dielectric properties are most probably discontinuous at the interfaces.

1. Variation with time: The voltage associated with the double layer at each electrode will vary with time since the dielectric is mobile and the charges can wander around or discharge as a function of time. Even a mica capacitor, if left indefinitely in charged condition, will probably show a variation in voltage as a function of time. The more or less constancy of the open circuit voltage of H_2/O_2 cells consisting of ion-exchange membranes may be due to the fact that the immobile ion-exchange membrane dielectric prevents or reduces the discharge of the double layer.

2. The chemical and the physical nature of the electrode will influence both the total area as well as the type of adsorption and therefore the thickness of the double layer at each electrode and will, therefore, influence ΔV_c. Different metallic surfaces will also exhibit different degrees of specificity for ionic adsorption, and consequently, q will be different.

3. Electrolyte pH and concentrations of various electrolytes. The charge q will depend on the type and concentration of various ions. Thus, for instance, OH^- ions have much greater polarizability than H^+ ions and will show greater specific adsorption depending on the electrode material and activity.

4. Effect of foreign anions: It is an experimental fact that polarizable anions, especially chloride, bromide and iodide ions are preferentially adsorbed at the electrode-electrolyte interface. This specific adsorption is expected to reduce the charge density because of their larger sizes and also the double layer thickness at each electrode-electrolyte interface. The reduction in q and the double layer thickness will decrease the electrostatic potential across the capacitor.

The extent of specific adsorption will depend, among other factors, on the polarizability of the foreign ions. The effect of the halide ions of different polarizability on the oxygen electrode potential can thus be interpreted in terms of their specific adsorption which increases with the polarizability of the ions involved. The halide ions (except F^-) may also participate electrochemically giving rise to a mixed potential due to two simaltaneous electrochemical reactions.

5. Effect of the concentration of foreign ions: The smaller the concentration of the specifically adsorbable anions, the smaller will be the number of active sites occupied by these foreign ions, hence the smaller the gross effect. This is shown by the concentration effect experimentally observed (Table 7). That a change in concentration of these ions shows its effect on the double layer capacity for polarized platinum electrode is reported by Popat and Hackerman (65).

6. Stirring or agitation of the electrolyte will disturb the charge distribution at each electrode-electrolyte interface and thus affect ΔV_c.

7. Effect of total area under the electrolyte: The smaller the area of the electrode (for the same charge), the larger the ΔV_c. It is experimentally observed that if the electrode is partly pulled out of the solution, the voltage goes up by several millivolts. If the electrode is again immersed in the solution, the voltage goes down again as expected.

8. Transient "anomalous" open circuit voltage greater than 1.23V. This is caused by two factors: a) The difference in the concentration of the electroactive species or pH at each electrode. Thus, if the pH at the hydrogen electrode is alkaline and that at the oxygen electrode is acidic, the open circuit voltage of such an H_2/O_2 cell will be greater than 1.23V and the exact value will depend, among other factors, on ΔpH. This aspect has been discussed in the preceding section. The cell potential also depends on the type of electrode material and the surface activity. Thus, for instance, with bright Pt, the V_{oc} is only about 1.4V compared to 1.82V with platinum black. It may be noted that anodic pre-electrolysis will make the pH at the anode surface more acidic, and therefore the oxygen electrode potential exhibited will be greater than the normal value. If the open circuit voltage across both the test electrode and the auxiliary (counter) electrode is measured after pro-longed electrolysis, it will be different from the initial value and may be attributed to the concentration gradient. (b) Factors other than pH, for instance water repellant treatment will change (reduce) the effective dielectric constant and also change the chemisorption properties at each electrode.

9. **Anomalous effect of temperature:** The dielectric constant of the dielectric medium usually decreases as the temperature is raised. Thus, the dielectric constant of water decreases with temperature as follows (66):

Temp (°C)	0	10	20	30	40	50	60	70	80	90	100
Dielectric Constant	88	84.11	80.36	76.75	73.28	69.94	66.74	63.68	60.76	57.98	55.33

An increase in temperature will therefore decrease the dielectric constant of the electrode-electrolyte interface, thus resulting in an increase in the open circuit voltage. It may be noted that for fused salts, the effect on V_{dl} will be more enhanced since the dielectric constant for fused salts like $NaNo_3$ will not be greatly different from the value of 5 for solid $NaNo_3$. An increase in temperature will also change the properties of each electrode-gas-electrolyte interphase as well as the ionic conductivity of the electrolyte. Under open circuit conditions these changes are expected to be of relatively minor importance compared to the dielectric properties of the electrolyte.

The variation of V_{oc} with water-repellant treatment, with changes in electrode areas, and spacing and other operational parameters may be interpreted in terms of changes in ΔV_c at or near the open-circuit conditions provided these parameters do not significantly affect V_g and ΔV_{irr}.

In view of the enormous complexity and interdependence of these variables and in absence of more definitive or quantitative data, the present interpretation must be considered tentative and to a certain degree speculative.

Some Conclusions:

On the basis of the experimental data summarized here it is suggested that (a) under the practical operating conditions of an H_2/O_2 fuel cell, an IR-free, steady-state voltage greater than approximately 0.93V is not likely to be achieved. The extrapolated, and nearly constant IR-free polarization loss of approximately 0.3V appears to be a specific property of the H_2/O_2 fuel cell systems or of OH^- ions since it is apparently unaffected by the usual rate or kinetic parameters. This irreversibility is tentatively attributed to the inherent, unavoidable pH gradients associated with current flow. An energetic interpretation in terms of established thermodynamic functions is suggested. (b) Platinum black appears to be the best catalyst for the oxygen electrode, and judging from the essentially zero slope of the IR-free linear plots over a fairly large range of current density, it would appear that a catalyst more effective than Platinum black is not likely to be found since inherent thermodynamic irreversibility cannot be reduced or eliminated by catalysts.

(c) Various existing theories of the irreversibility of the oxygen electrode have been reviewed and it is shown that none of these can satisfactorily explain all the experimental observations concerning the open-circuit behavior of the oxygen electrode. A tentative interpretation based on double layer capacitance effects is proposed for the irreversibility of the oxygen electrode at or near the open-circuit conditions. (d) It is shown that by properly buffering the pH in the vicinity of each electrode, open-circuit voltages greater than 1.23 volts can be attained. The additional voltage however, cannot apparently be used as a source of steady emf or electrical energy.

Some possible objections to the proposed interpretation:

Several possible objections to the suggested interpretation can be raised:

1. The peroxide intermediate as a possible source of polarization is not definitely ruled out though its relative insensitivity to rate parameters, 100% faradaic efficiency based on 4 faradays per mole of O_2, failure to isolate any H_2O_2 in operating fuel cells and uncertainty of applying the Nernst equation suggest an absence of the peroxide mechanism as a major cause of polarization loss.

2. The postulated pH gradients as a cause of irreversibility do not appear to be in complete harmony with the calculations using Fick's law of diffusion and the diffusion coefficients. Fick's law of diffusion is strickly applicable only under the conditions of pure and free diffusion under concentration gradients and in the absence of any electrical migration or specific adsorption forces. In practice this requires extremely large concentration of inert electrolyte and comparatively small concentrations of electroactive species. These conditions do not obtain for the fuel cell systems considered here. The value of the diffusion coefficients for concentrated acids and bases used here are also unknown since its evaluation assumed an infinitely dilute solution.

3. Perhaps the most serious objection is that the present study attributes irreversibility to the electrochemical properties of the entire H_2/O_2 fuel cells, whereas the existing views attribute the irreversibility to the oxygen electrode alone. This aspect needs further experimental work. The problem of measuring unambiguously each electrode potential in operating H_2/O_2 fuel cell has already been discussed. However, if it can be definitely established that the hydrogen electrode does behave reversibly in acidic as well as alkaline media in an operating H_2/O_2 fuel cell, then the irreversibility of the oxygen electrode must be attributed to the specific properties of OH^- ions together with those of oxygen rather than to any rate-limiting steps involving activation polarization.

Only further experimental work can clarify this aspect.

10.0 Recommendations for Future Work:

1. Establish the validity of the use of various reference electrodes or probes for measuring the potential of the oxygen electrode under open circuit and current flow conditions.

2. Study the behavior of the oxygen electrode in the non-linear region of the polarization plots as a function of time, pH, electrode material and other parameters in conjunction with a suitable reference electrode.

3. Confirm and extend to higher current densities, the linear sections of the polarization plots with and without IR corrections, and compare this with the polarization characteristics during charging i.e. electrolytic evolution of H_2 and O_2.

4. Determine the pH and temperature profiles at each electrode as a function of electrolyte pH and current density and correlate this with thermodynamic predictions.

5. Establish whether an acid/base concentration cell discharge involves faradaic (i.e. redox) or non-faradaic (i.e. capacitor-type) current. Investigate the nature and the contribution of the electrical double layer capacitance effects to the oxygen electrode behavior on open circuit and in the non-linear region of the polarization plots.

11.0 LITERATURE REFERENCES

References

1. Latimer, W. T. "Oxodation Potentials." Second edition; p. 39, Prentice Hall (1952).

2. Pawlowski, A. T. M. S. Thesis, Boston College, Boston,(May 1956).

3. Ives, D. J. G. and Janz, G. J., Reference Electrodes, p. 11 Academic Press (1961).

4. Langmuir I. Trans. Electrochem. Soc., XXIX, p. 293 (1916).

5. Muller, O. H. The Polarographic Method of Analysis, p. 11 Chemical Education Publishing Co., Easton, P. (1951).

6. Lingane, J. J. Electroanalytical Chemistry; Second edition; p. 41, Interscience Publishers, Inc., New York (1958).

7. Hacobian, S. Australian J. of Chemistry; 6, p. 211 (1953).

8. Potter, E. C. Electrochemistry, Principles and Applications, p. 91, Cleaver-Hume Press Ltd., London (1956).

9. Kortum, G. and Bockris, J. O'M. Textbook of Electrochemistry Vol. II; p. 581 (1951), Elsevier Pub. Co., New York (1951).

10. See Reference 3, p. 72.

11. See Reference 3, p. 73.

12. Grubb, W. T. and Niedrach, L. W.; J. Electrochem. Soc.; 107, 133, (1960).

13. Kordesch, K. and Marko, A.; J. Electrochem. Soc.; 107, 480 (1960).

14. F. T. Bacon, Private Communication.

15. Justi et. al. "High Drain Hydrogen Diffusion Electrodes Operating at Ambient Temperature and Low Pressure" (Translation from original German); p. 242, Fig. 118, Curve C, Franz Steiner Verlag GmbH Wiesbraden, Germany (1959).

16. Elmore, G. V. and Tanner, H. A.; J. Electrochem. Soc.; V. 108, 669 (1961).

17. Stein, B. R. and Cohn, E. M., "Second Status Report on Fuel Cells" Army Research Office, Report No. 2, p. 61 (1961).

18. Knobel and Joy; Trans. Electrochem. Soc.; V. 44, 443 (1923).

19. Richards, W. T.; J. Phy. Chem.; V. 32, 990 (1928).

20. Hauel, R & D Div. Engelhard Industries: Newark, N. J.; Second Quarterly Report on"Fuel Cell Catalysts" to U.S. Army Signal R & D Laboratories; Cont. No. DA-36-039-SC-85043.

21. Smale, F. J. Z. Physik, Chem.; V. 14, 577 (1894).

22. Bain, H. G.; Trans. Electrochem. Soc.; v. 78, 173 (1940).

23. Bockris, J. O'M and Huq, A.K.M.S.; Proc. Roy. Soc. A, 237, 277-296 (1956).

24. Barnartt, S., J. Electrochem. Soc.; V. 106, 726 (1959).

25. Mantell, C. A., Industrial Electrochemistry, Second edition; Chapter IV; p. 76-77, McGraw Hill Book Co.; New York (1940).

26. Bennewitz; Zeit Physik, Chem.; V. 72, 223 (1910).

27. DeBethune, A. J., Ind, and Eng. Chem. 50, 129 (1958).

28. Patric, W. A. and Wagner, H. B., Corrosion, 6, 34 (1950).

29. See for instance, Stender, W. W. and Seerak, I. J., Trans. Electrochem. Soc., LXVIII,493-520 (1935).

30. See Ref. 31.

31. Reed; Trans. Electrochem. Soc., IV, 151, (1904).

32. Schoch, E. P., J. Phy. Chem., 14, 665 (1910).

33. Hoar, T. P., Proc. Royal Soc., (London), 142, 628-648 (1933).

34. Mond, L. and Langer, C., Proc. Royal Soc., (London) Vol. 46, 296 (1889).

35. Uhlig, H. H., Z Elektrochem. 62, Nr 62, p. 626 (1958).

36. Kolotyrkin, Y. M., Z. Elektrochem. 62, 664 (1958).

37. Giner, J., ibid, 63, 386 (1959).

38. Popat, P. V. and Hackerman, N. H., J. Phy. Chem. (in press).

39. Evans, U. R., Z. Elektrochem. 62, 619 (1958).

40. Bonhoeffer, K. F. and U. F. Frank, Z. Elektrochem. Angew Physik. Chem. 55, 180, (1951).

41. Velter, K. J., ibid 55, 675, (1951).

42. Lingane, J. J.

43. Laitinen and Enke, J. Electrochem. Soc. 107, 773 (1960).

44. Chapman and Reynolds; Proc. Roy. Soc., A 156, 284 (1936).

45. Armstrong, Himsworth and Butler, ibid, A 143, 89 (1933).

46. Moeller, T., Inorganic Chemistry; p. 888, John Wiley and Sons, New York (1952).

47. H. Cohen, R. A. Rischer, E. Tomozsko and J. G. Aston; Paris Conference on Catalysis; peper 3, (1960).

48. Hoar, T. P., International Committee on Electrochemical Thermodynamics and Kinetics; 8th meeting; 1956; Published by Butterworths, p. 439 (1958).

49. Traube, M., Ber. Deutsch, Chem. Ges. 15, 659, 2434 (1882).

50. Iofa, Z. A., Moiseeva, N. B., Mirlina, S., Ya and Krymakova, E. E., Zhur, Priklad., Khim; 21, 329, (1947); C. A. 44, 9276 d.

51. Berl, W. G., Trans. Electrochem. Soc., 83, 253 (1943).

52. Witherspoon, R. R., Urbach, H; Yeager ,E, and Hovorka, F., "Oxygen Electrode," Technical Report No. 4 to office of Naval Research, Contr. No. Nonr 581 Oct. (1954).

53. Yeager, E. et. al. Paper presented at the Oct. 1961 Meeting of the Electrochem. Soc., Detroit, Extended Abstract No. 24, p. 14.

54. Kordesch, K., in "Fuel Cells;" editor G. J. Young; Reinhold Publishing Corp. (1960).

55. Weise, R. S. and Jaffe, S. S., Trans. Electrochem. Soc., 93, 128, (1948).

56. Winkelmann, D., Z. Elektrochem. Bd 60, No. 7; 731 (1956).

57. Vielstich, W., Z. Physik. Chem. NF. 16, p. 409 (1958).

58. Gerischer, R. and Gerischer, H., ibid 178 (1956).

59. Hikling A. and Wilson, W. H., J. Electrochem. Soc., 98, 425, (1951).

60. Barak, M., Gillibrand, M. I., and Gray, J. Paper presented at the Battery division, Electrochem. Soc., Detroit, Michigan, Oct. 4, 1961, Abstract No. 22.

61. Justi, E. W., and Winsel, A. W., Paper presented at the Electrochem. Soc. Meeting, Indianapolis, May, 1961, Abstract No. 103.

62. Young, G. J. and Rozelle, R. B., J. Chem. Ed., 36, 68-73 (1959).

63. DeBoer, J. H. Advances in Catalysis, Vol. VIII, p. 18 (1956).

64. Adam, N. K., "The Physics and Chemistry of Surfaces," Oxford Univ., Press Third edition, p. 236 (1941).

65. Popat, P. V. and Hackerman, N., J. Phy. Chem. 62, 1198 (1958).

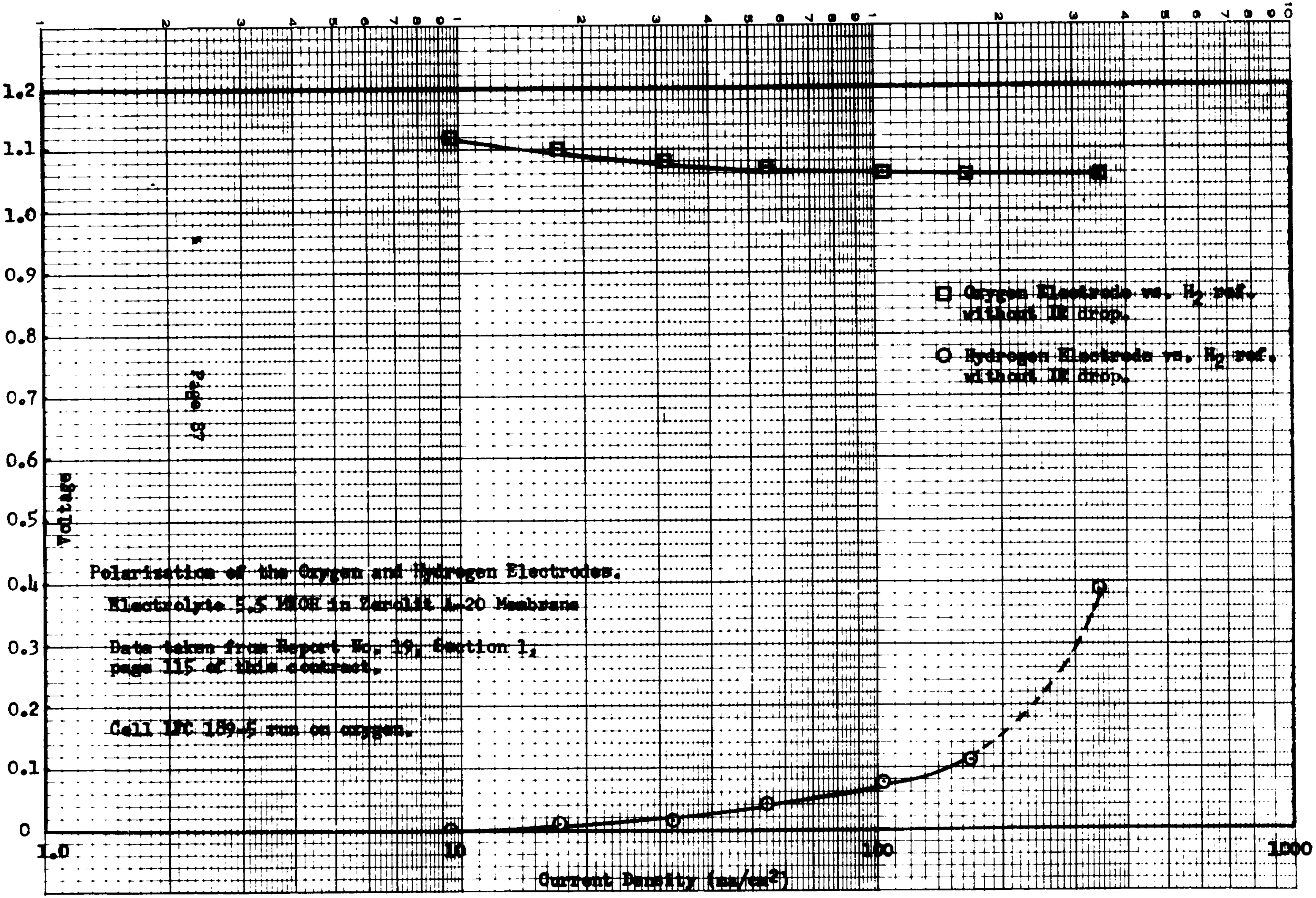
66. Handbook of Chemistry and Physics, Chem. Rubber Publishing Co. 40th Edition, p. 2523.

67. Niedrach, L.W., and Gilman, S., Final Report on Ion-Exchange Regenerative Fuel Cell Research and Dev. Program. ASTIA AD-248-480, from G.E. Co., Philadelphia, Pa., Sept. 1960.

12.0 APPENDIX A

NO. 340R-L310 DIETZGEN GRAPH PAPER
SEMI-LOGARITHMIC 3 CYCLES X 70 DIVISIONS

EUGENE DIETZGEN CO.
MADE IN U S A



Polarization of the Oxygen and Hydrogen Electrodes.

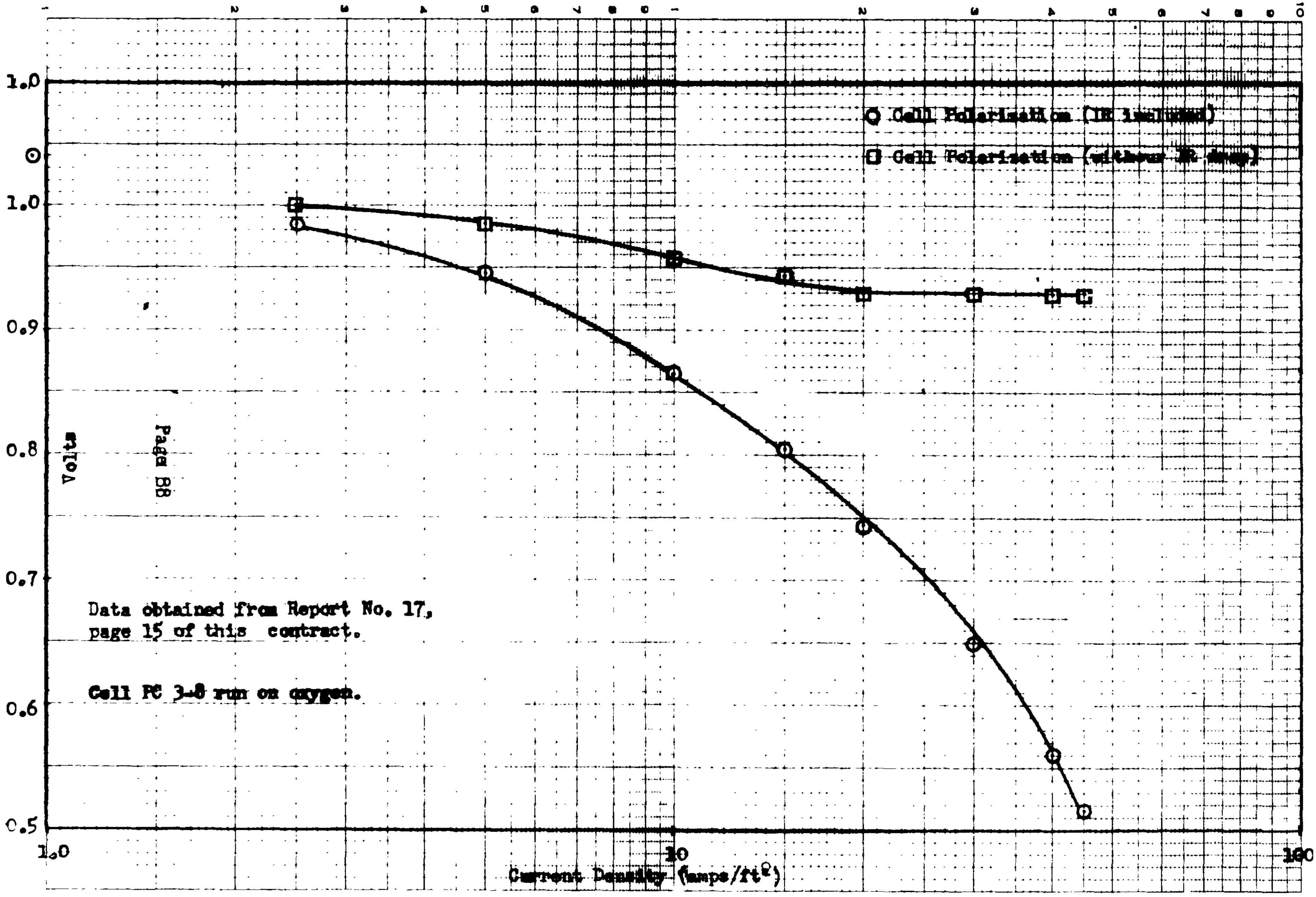
Electrolyte 5.5 NKOH in Zerolit A-20 Membrane

Data taken from Report No. 19, Section 1, page 115 of this contract.

Cell LPC 189-5 run on oxygen.

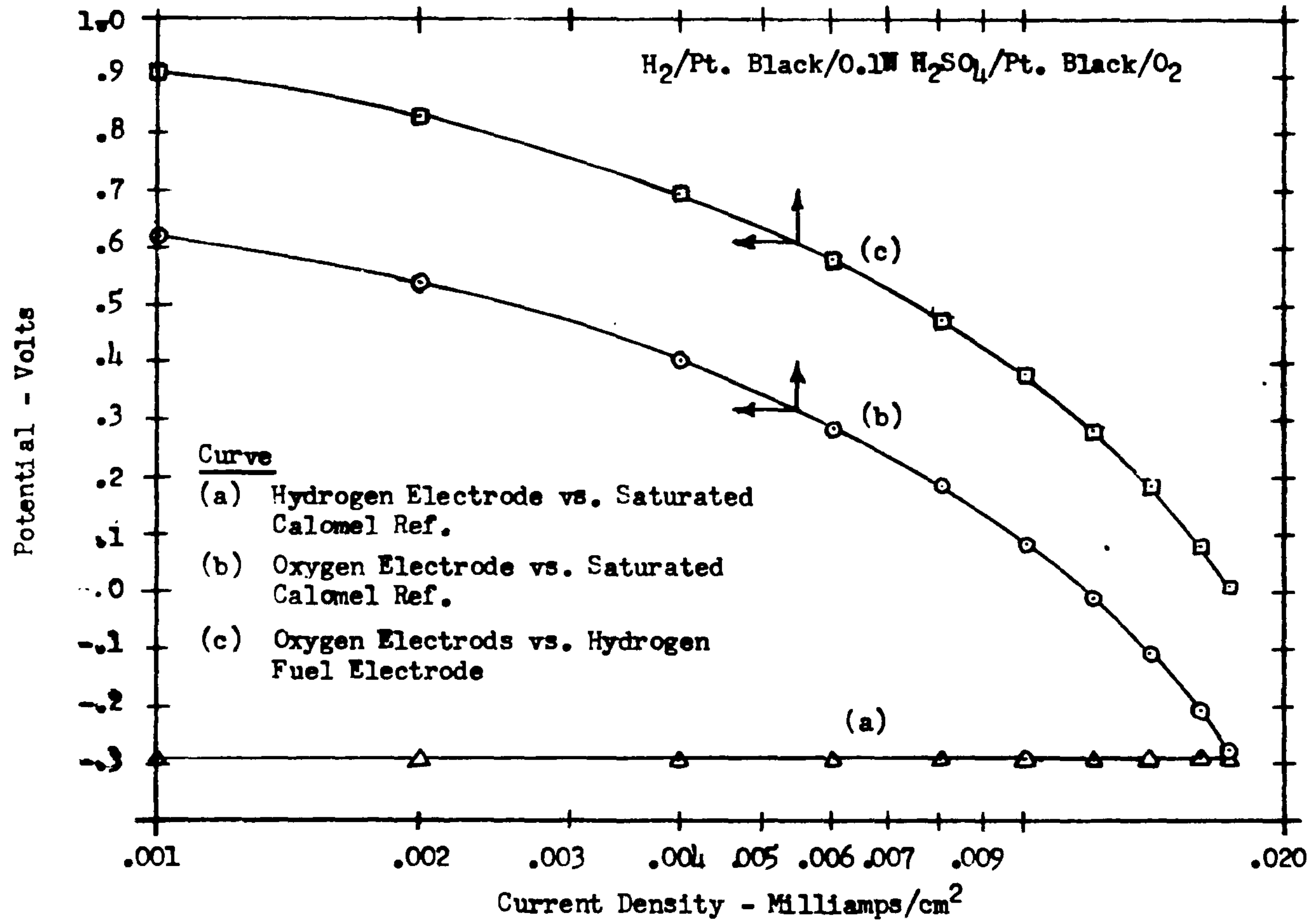
10 340R DIETZGEN GRAPH PAPER
SEMI-LOGARITHMIC
2 CYCLES X DIVISIONS PER INCH

EUGENE DIETZGEN CO.
MADE IN U.S.A.



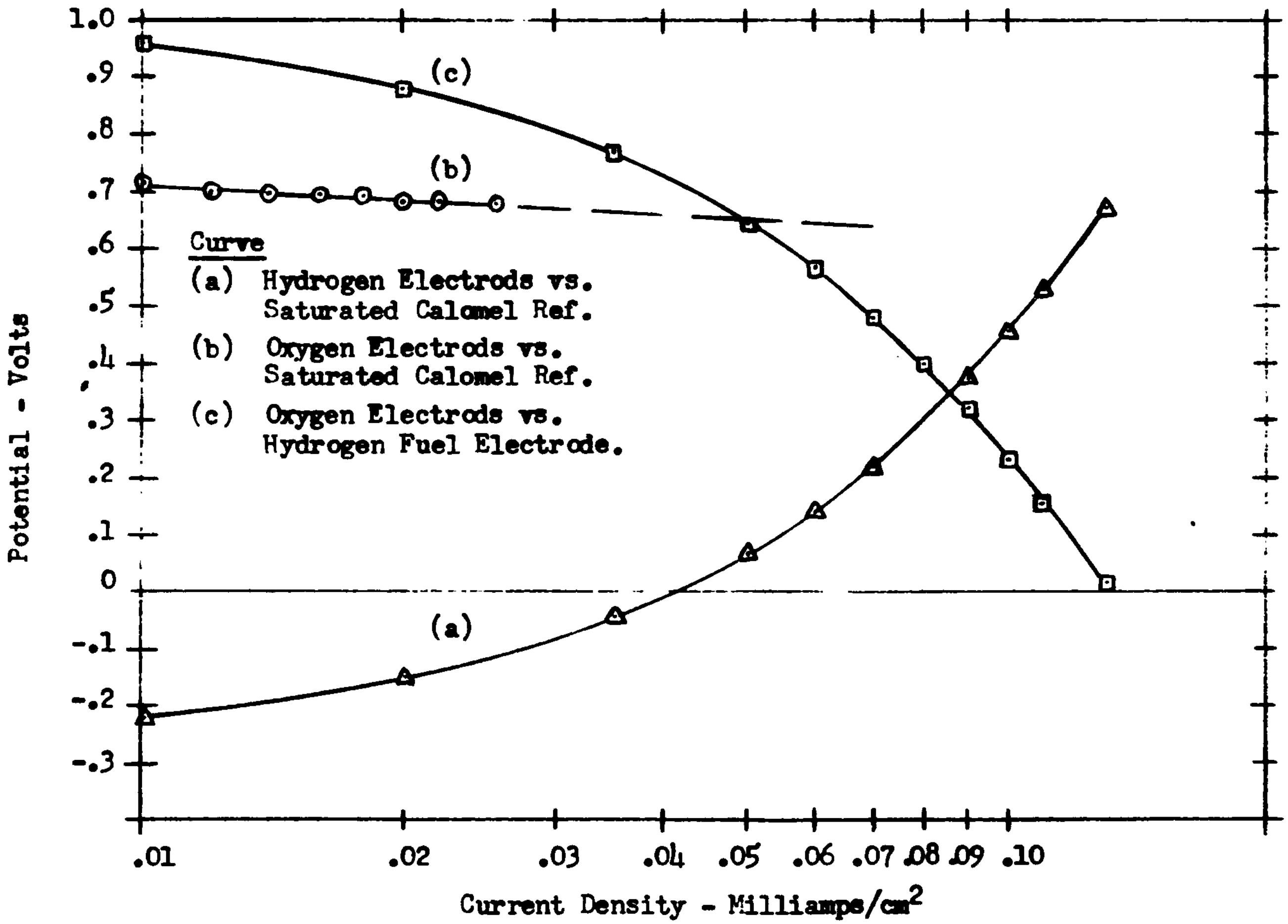
Data obtained from Report No. 17,
page 15 of this contract.

Cell FC 3-8 run on oxygen.



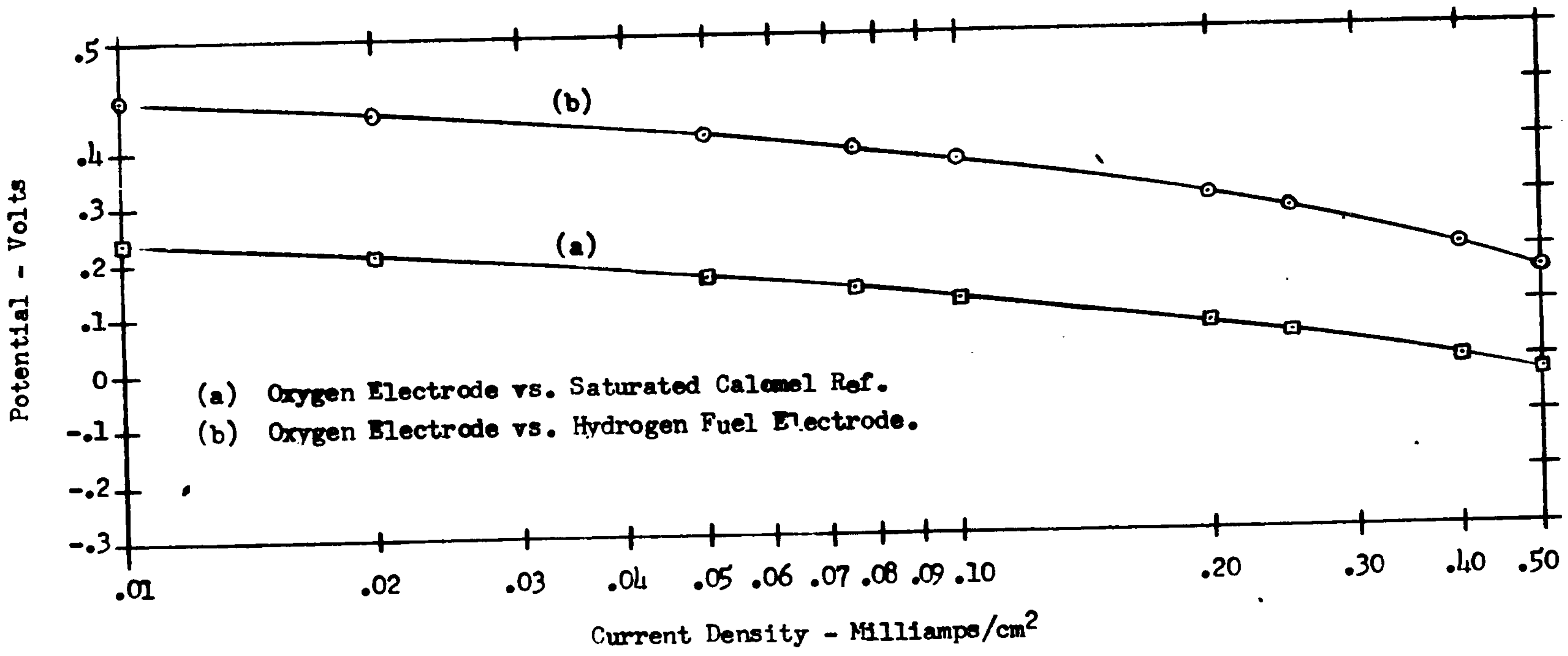
Oxygen Electrode Polarization for Platinized
Platinum in Aqueous Electrolyte

Appendix A



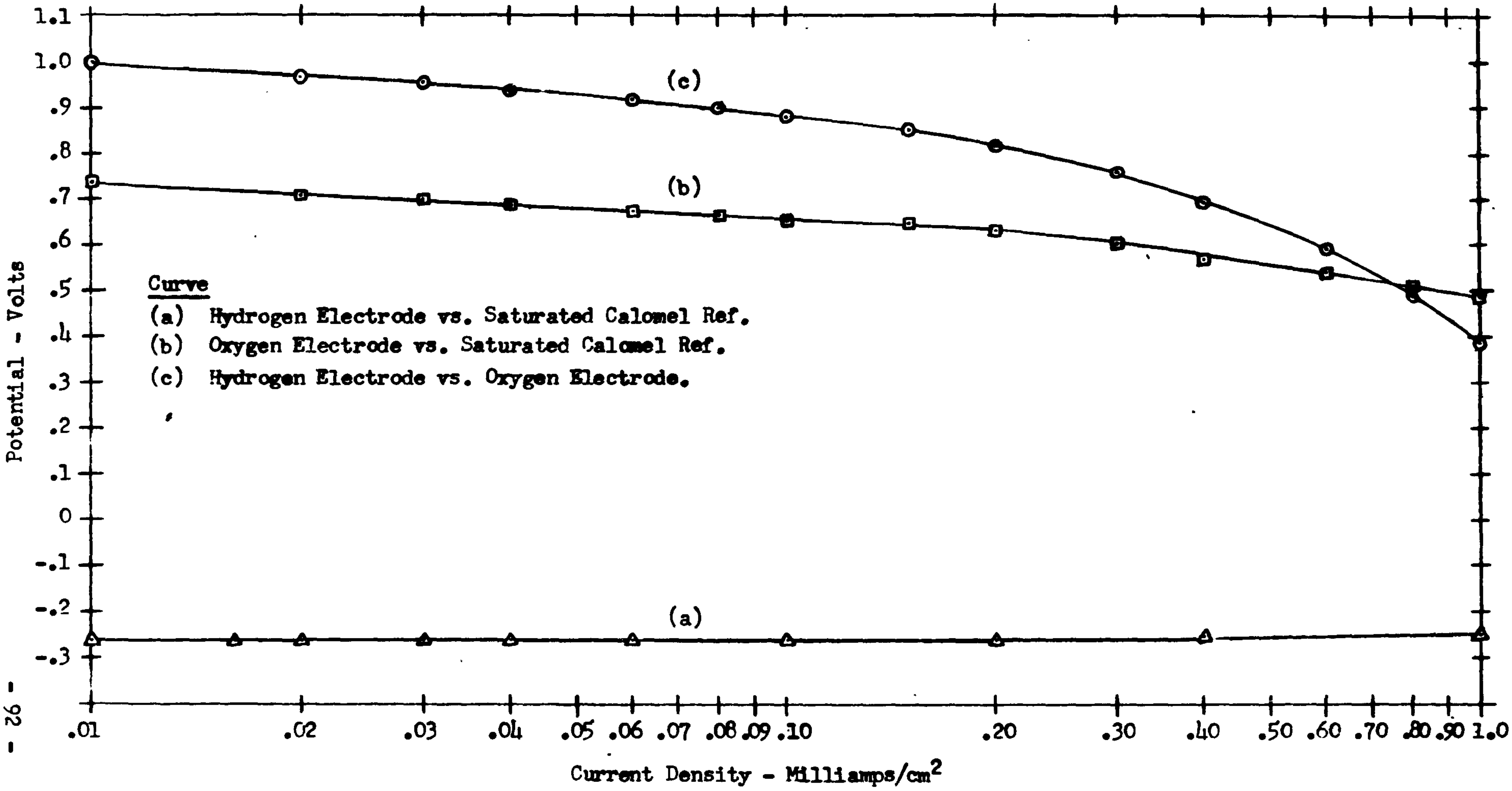
Hydrogen Electrode Polarization for
Platinized Platinum Electrode in 0.1 N H_2SO_4

Appendix A



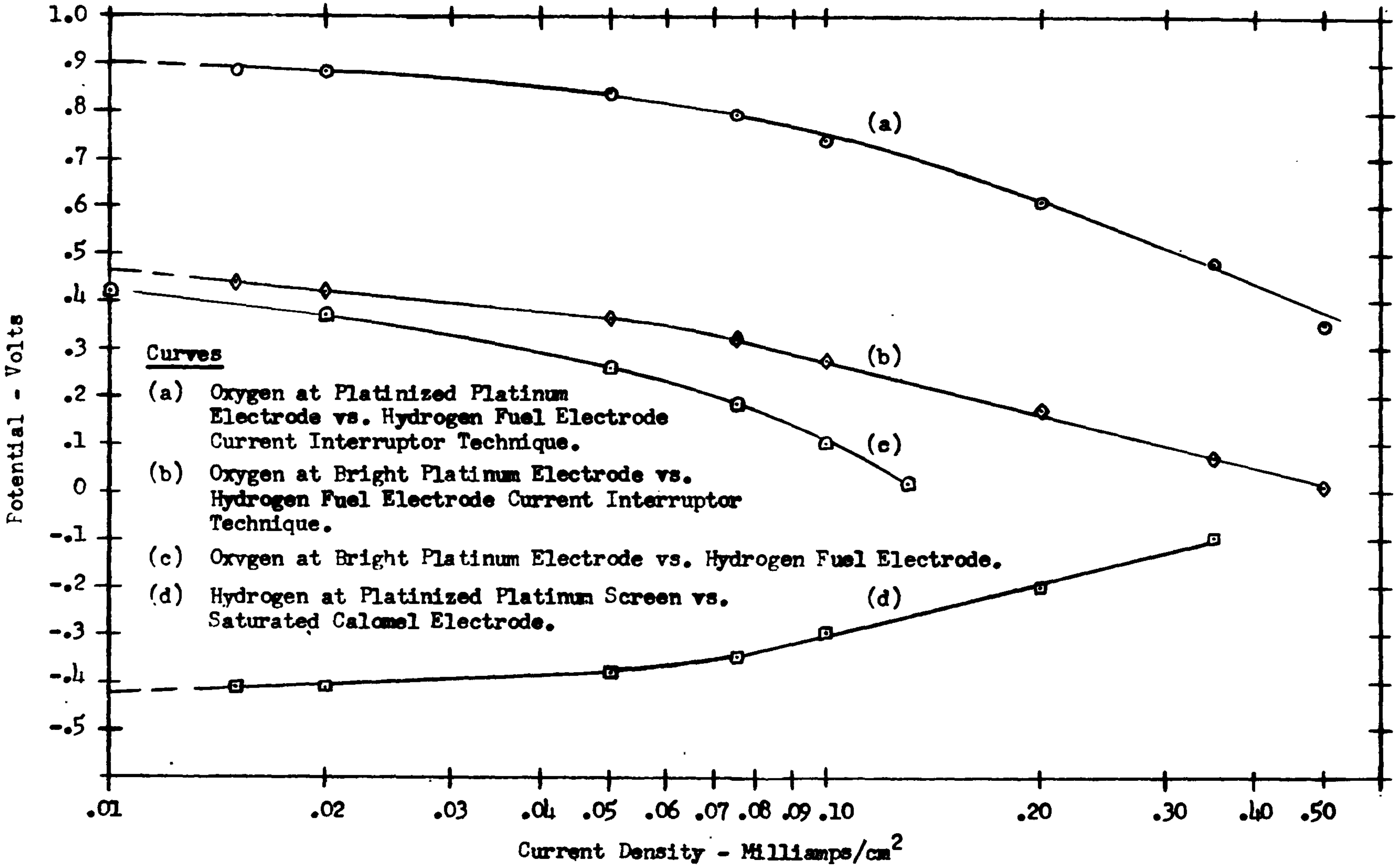
Oxygen Electrode Polarization for Bright Platinum in 1.04 N H_2SO_4

Appendix A



Oxygen Electrode Polarization for Platinized Platinum in
1.04 N H_2SO_4 (O_2 & H_2 Electrodes of Equal Area)

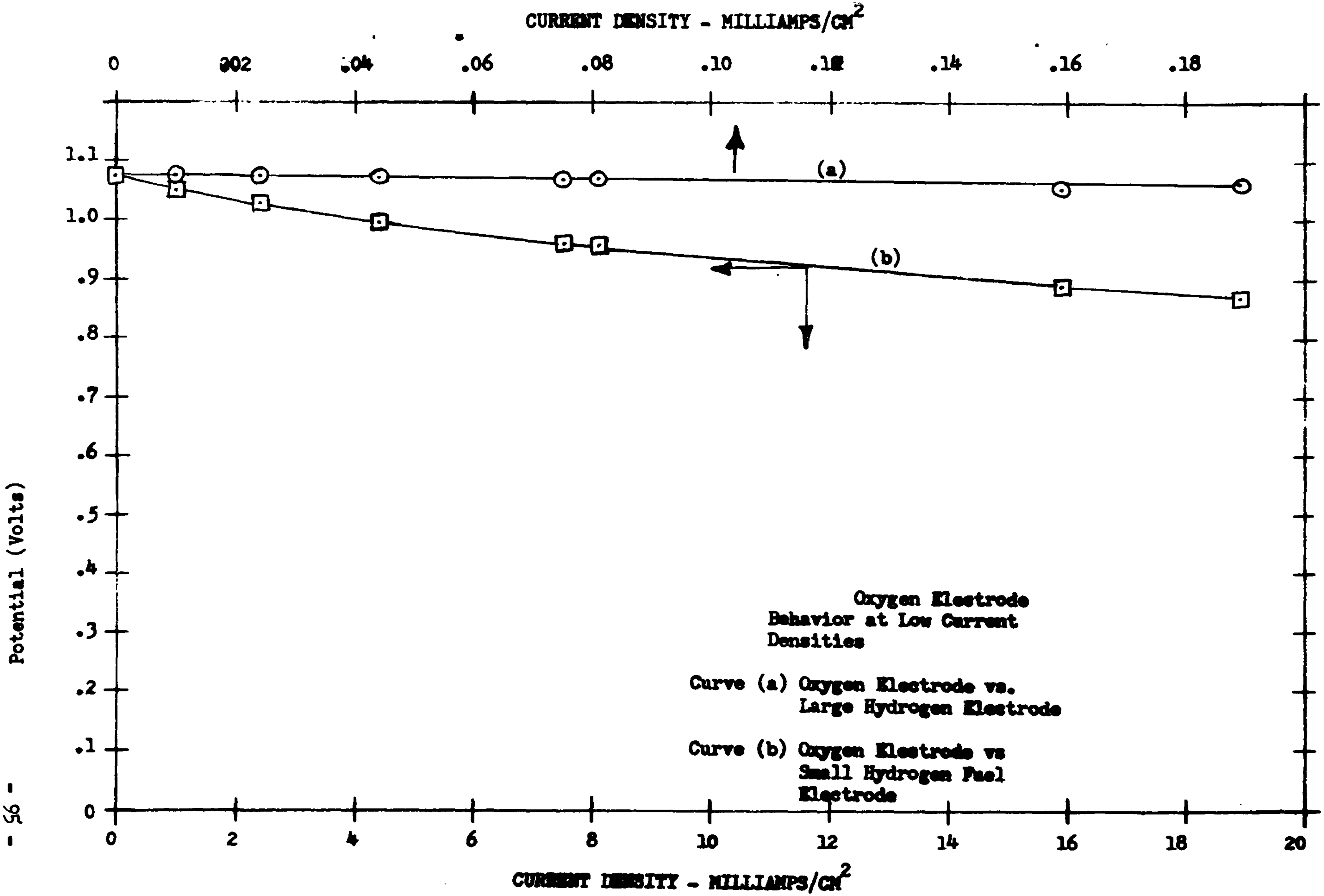
Appendix B



Polarization of Hydrogen & Oxygen Electrodes
in Sodium Acetate-Acetic Acid Buffer (pH = 4)

Appendix B

13.0 APPENDIX B

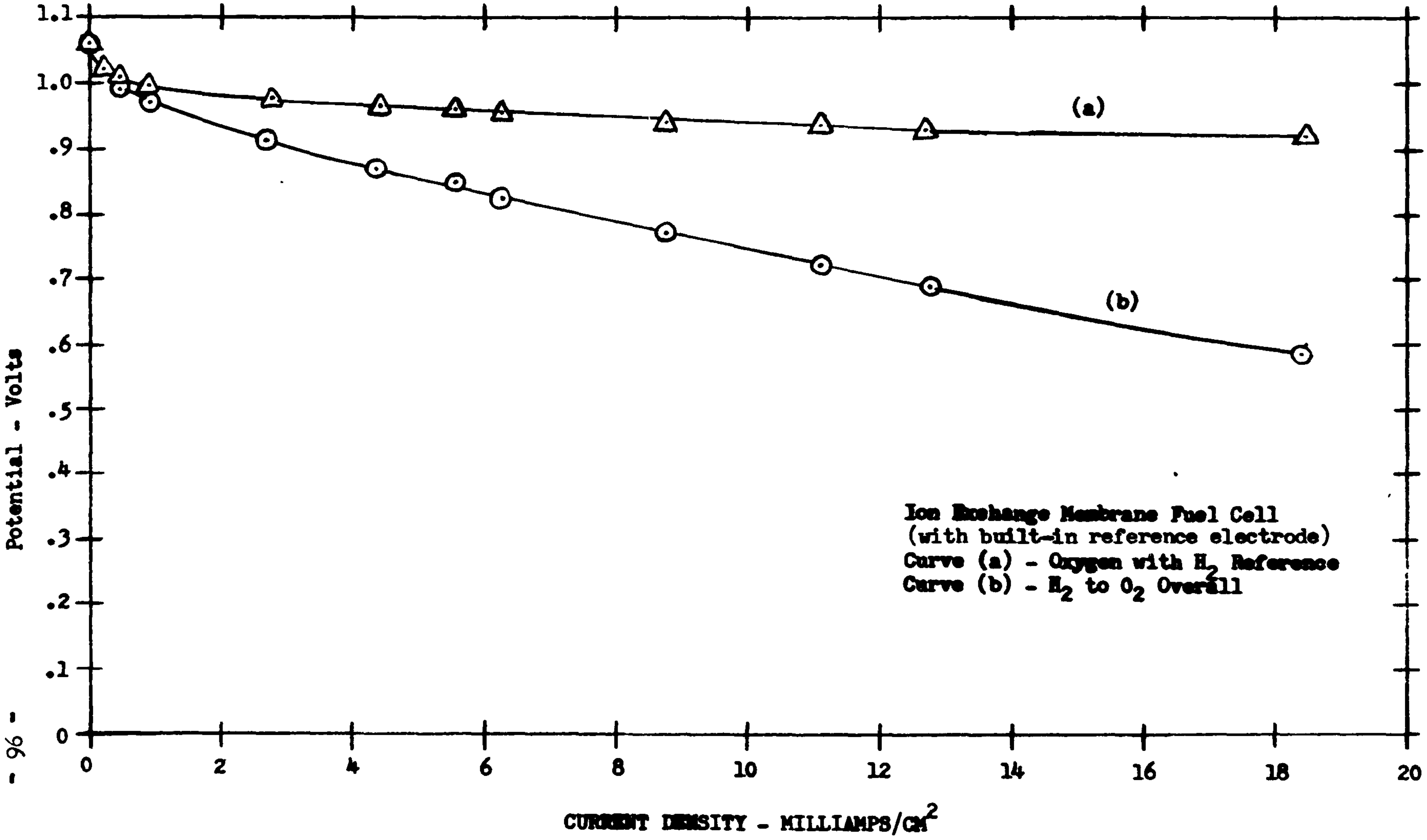


Oxygen Electrode
Behavior at Low Current
Densities

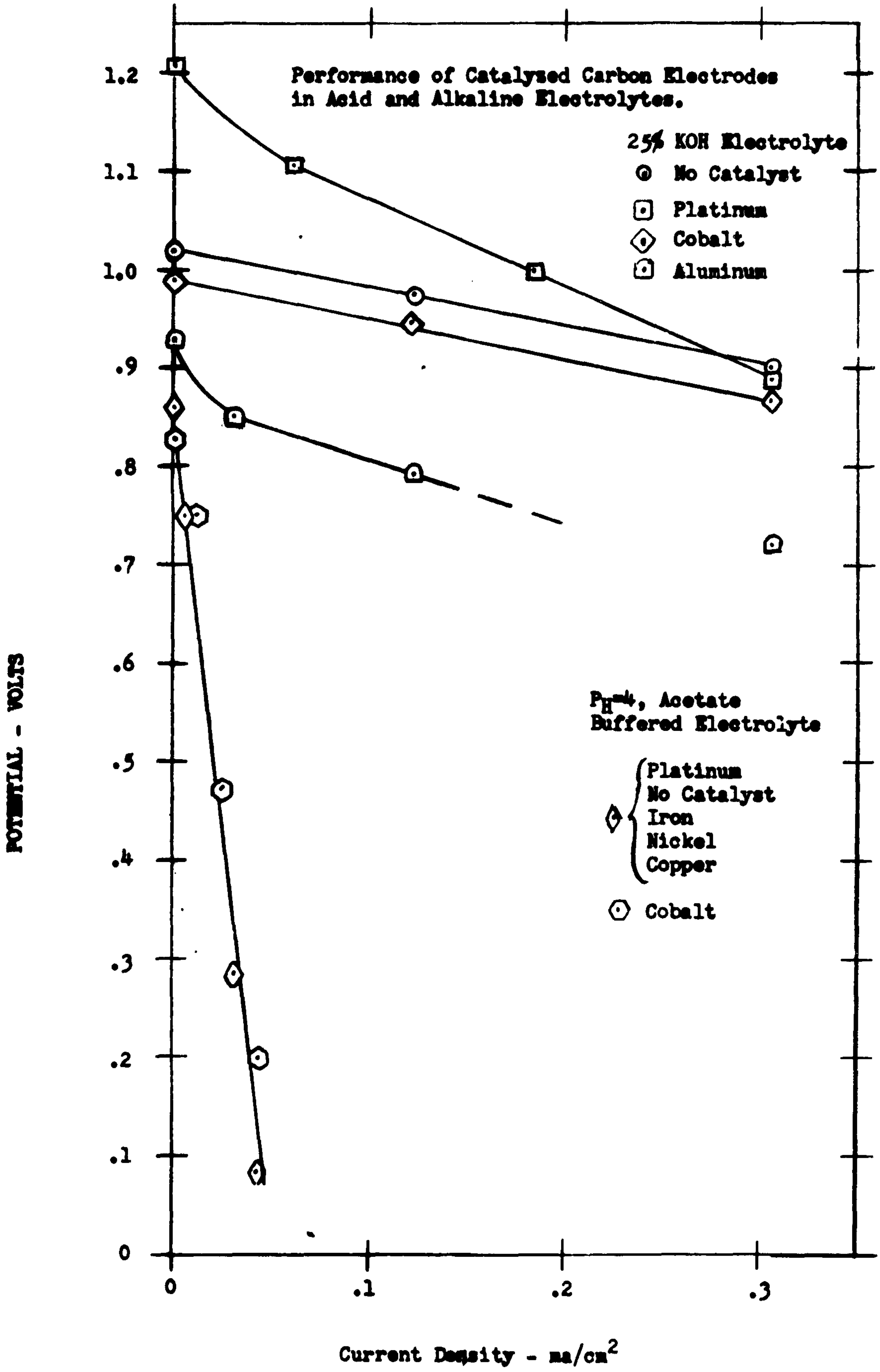
Curve (a) Oxygen Electrode vs.
Large Hydrogen Electrode

Curve (b) Oxygen Electrode vs
Small Hydrogen Fuel
Electrode

Appendix B

1.1
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
0
Potential - Volts
0
2
4
6
8
10
12
14
16
18
20
CURRENT DENSITY - MILLIAMPS/CM^2
(a)
(b)
Ion Exchange Membrane Fuel Cell
(with built-in reference electrode)
Curve (a) - Oxygen with H_2 Reference
Curve (b) - H_2 to O_2 Overall

Appendix B


Performance of Catalysed Carbon Electrodes in Acid and Alkaline Electrolytes.
25% KOH Electrolyte
No Catalyst
Platinum
Cobalt
Aluminum
$P_H=4$, Acetate Buffered Electrolyte
Platinum
No Catalyst
Iron
Nickel
Copper
Cobalt
POTENTIAL - VOLTS
1.2
1.1
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
0
0
.1
.2
.3
Current Density - ma/cm^2

Appendix B

14.0 APPENDIX C

APPENDIX C

TABLE I

Effect of Materials and Methods of Wet-proofing on the Polarization Characteristics of the oxygen electrode in alkaline solution.

Electrode: Carbon from Stackpole Carbon Co., 5/8" dia. 1" long; (about 15 cm^2); treated at 800°C for 5 minutes, quenched and dried at 800°C for 2 minutes.

Catalyst: Platinum black from chloroplatinic acid; after soaking electrode overnight, reduced at 300°C for 4 hours; after cementing the holder, treated at about 200°C overnight.

Electrolyte: 25% KOH.

Electrode Number	Type Carbon	Wet-proofing Material	Method of Wet-proofing	Polarization			Remarks
				Time (Minutes)	Ma	Volts	
1	PC 53H	2% paraffin wax in petroleum ether	300°F, 1/2 hr.		0.0	1.07	Voltage dropping continuously
6	PC 53H	30% Teflon	300°F, 3 hrs.	0 2 14	0.00 0.00 0.00	0.91 0.93 0.980	
7	PC 53H	2% paraffin in toulene	300°F, 1/2 hr.	0 4 8	0.00 0.00 0.00	1.08 1.07 1.08	
12	219XG	2% paraffin in petroleum ether	300°F, 1/2 hr.	0 1 2 5	0.00 0.00 0.00 0.0	1.08 1.06 1.055 1.030	
14	219XG	2% paraffin	300°F, 1/2 hr.	0	0.0	1.17 (dropping)	No heating before catalyst applicatio

APPENDIX C (Cont'd)

TABLE I

Electrode Number	Type Carbon	Wet-proofing Material	Method of Wet-proofing	Polarization Time (Min.)	Ma	Volts	Remarks
15	2 24XG	2% paraffin in petroleum ether	300°F, 1/2 hr.	0 5 13	0.0 0.0	1.01 0.997 0.995	Cracks in the electrode
17	224XG	2% paraffin in petroleum ether	300°F, 1/2 hr.	0 5	0.00 0.00	1.12 1.07	
16	PC53H	2% ceresine in petroleum ether	300°F, 1/2 hr.	0 overnight	0.0 0.0	0.87 0.92	
20	224XG	2% ceresine in petroleum ether	300°F, 1/2 hr.	00 10	0.0 0.0	0.87 0.88	
17	219XG	2% ceresine in petroleum ether	300°F, 1/2 hr.	0 2 3 6 16 21 23 20 55 75 - -	0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 10 21	0.99 1.03 1.045 1.060 1.090 1.102 1.105 1.108 1.097 1.075 0.53 0.105	
3	219XG	1% Zelan in isopropanol Repeated experiment	300°F, 1/2 hr.	0 5 13 0 8	0.00 0.0 0.0 0.0 0.0	1.01 0.985 0.990 1.10 1.10	

APPENDIX C (Cont'd)

TABLE I

Electrode Number	Type Carbon	Wet-proofing Material	Method of Wet-proofing	Polarization			Remarks
				Time (Min.)	Ma	Volts	
13-1	219XG	None		0	0.0	0.928	
				16	0.0	0.982	
				34		0.992	
				47		0.997	
				92		0.997	
15	219XG	Carnauba Wax	300°F, 1/2 hr.	0	0.0	0.953	
				4	0.0	0.976	
				10		0.987	
				19	0.0	0.999	
				25	0.0	1.005	
				30	0.0	1.000	

APPENDIX C (Cont'd)

TABLE II

Effect of Teflon wet-proofing on oxygen electrode polarization.

Electrode: 219XG Stackpole carbon, treated in the same manner as described in TABLE I.

Catalyst and electrolyte are the same as in TABLE I.

Wet-proofing: 10% Teflon suspension, cured overnight at 200°C. (For earlier results with Teflon wet-proofing see the preceding Progress Report.)

Time (Min.)	Ma	Volts	Remarks
0	0	0.06	
1	0	0.09	
2	0	0.105	
4	0	0.140	
10	0	0.735	
32	0	0.916	
40	0	0.956	
82	0	1.002	
			Same electrode cleaned with emery paper, washed reheated at 350°C for 10 minutes and put in the test cell again.
1	0	1.230	
4	0	1.200	
7	0	1.160	
8	0	1.190	
9	0	1.196	
14	0	1.180	
	10	0.695	
	30	0.336	
	38	0.190	Put on open circuit.
0	0	6.90	
2	0	0.97	
8	0	1.00	
17	0	1.03	The electrode reheated to 350°C for five minutes.
0	0	1.183	Cooled and retested.
22	0	1.130	

15.0 ACKNOWLEDGEMENT

The author is grateful to the following scientists and engineers for stimulating discussions and suggestions during the course of this investigation:

Prof. Norman Hackerman of the University of Texas, Prof. A. J. deBethune of Boston College, Dr. G. J. Young representing ERDL; and Dr. D. L. Douglas, Dr. E. A. Oster, Dr. R. B. Hodgdon, Dr. H. J. Maget, Dr. E. J. Cairns, and Dr. T. W. Grubb of the General Electric Company. The results and conclusions were also discussed to some extent with Dr. J. B. Friauf of the Department of the Navy, Prof. R. M. Fuoss of Yale University, Dr. G. M. Schmid of Texas University, Dr. R. J. Brodd of the National Bureau of Standards, Dr. D. P. Gregory from Shell International Petroleum Co., Ltd., St. Helen's Court, London, and with other scientists and engineers.

DISTRIBUTION LIST

Mr. Marshall Aiken (1)
Department of the Army
Office of the Chief Signal Officer
Washington 25, D.C.
Attn: SIGRD-4a-3

Commanding Officer (1)
Office of Ordnance Research
U.S. Army Box CM
Duke Station
Durham, North Carolina
Attn: Mr. Park Espenschade

Mr. John Crellin (1)
Department of the Army
Office Chief of Ordnance
Pentagon
Washington 25, D.C.
Attn: ORDTB-F & L
Annex #2

Mr. Joseph Kaufman (1)
Department of the Army
Office Chief of Ordnance
Pentagon
Washington 25, D.C.
Attn: ORDTB-Res & Special Proj
Annex #2

Commanding General (2)
U.S. Army Signal Corps Research
& Development Laboratory
Power Sources Division
Fort Monmouth, New Jersey
Attn: Mr. A. F. Daniel

Mr. E. Cohn (1)
Office-Chief of Research & Engineering
Department of the Army
Room 3D442, Pentagon
Washington 25, D.C.

Armed Services Technical Information
Agency (10)
Arlington Hall Station
Arlington 12, Virginia
TISVR

Chief of Engineers (1)
Department of the Army
Washington D.C.
Attn: Mr. A. Goergens

Office of Ordnance Research (1)
Box CM
Duke Station
Durham, North Carolina
Attn: Internal Research Division

TRECOM (1)
Fort Eustis, Virginia
Attn: K.J. Loftheim
Research Directorate

Chief Bureau of Ships (1)
Code 675
Washington, D.C.

Chief Bureau of Ships (1)
Code 660S
Washington, D.C.
Attn: Mr. C. F. Viglotti

TRECOM (1)
Fort Eustis, Virginia
Attn: Dr. George Sands
Research Directorate-Physical
Sciences

California Research Corporation (1)
200 Bush Street
San Francisco 20, California
Attn: J.R. MacGregor

Commanding General (15)
U.S. Army Engineer Research and
Development Laboratories
Fort Belvoir, Virginia
Attn: Earl Cogswell - Electrical Power Branch

DISTRIBUTION LIST (Cont'd)

Mr. R. B. Goodrich (2)
Diamond Ordnance Fuse Laboratory
Ordnance Corps
Washington 25, D.C.
Attn: ORDTL-330-140

University of Florida (1)
Post Office Box 3027
University Station
Gainsville, Florida
Attn: Prof. R.D. Walker

Pennsylvania State University (1)
Fuel Technology Department
University Park, Pennsylvania
Attn: Prof. L.G. Austin

U.S. Naval Engineering (1)
Experiment Station
Annapolis, Maryland
Attn: Cord 712

Mr. Harry W. Fox (1)
Code 425-ONR
Washington 25, D.C.
Phone 11-61854